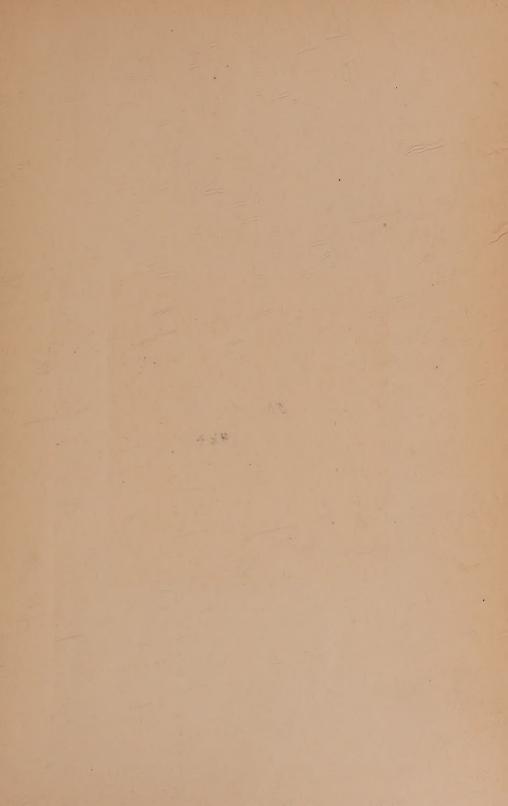


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# LEACHED OUTCROPS AS GUIDES TO COPPER ORE



# LEACHED OUTCROPS

AS GUIDES TO

# COPPER ORE

AUGUSTUS LOCKE



BALTIMORE
THE WILLIAMS & WILKINS COMPANY
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chalcopyrite and pyrite.  Botryoidal cavity linings correlated with mixtures of chalcocite and pyrite.  Halos and borders correlated with mixtures of sulphides rich in pyrite.  Halos and borders correlated with pyrite.  Limonite in various forms flooding the matrix correlated with pyrite.  Fluffy limonite replacing carbonates.  Fine limonite sponge replacing carbonate.  Coarse limonite sponge replacing kaolin.  Limonite clay replacing kaolin.  Jaspery limonite replacing kaolin.  Limonite in open spaces.  Temporary forms of limonite.  CHAPTER XII  ESTIMATION OF THE FORMER COPPER CONTENT.  CHAPTER XIII  USE OF THE RECONSTRUCTED SULPHIDE IN THE PREDICTION OF HIDDEN SULPHIDE.  CHAPTER XIV  SUMMARY AND CONCLUSION.		
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### CHAPTER I

### INTRODUCTORY

### THE WORK AND ITS PURPOSE

The cost of ore discovery in North America is acknowledged to be rising to dangerous heights and no argument is required to show that the early improvement of the orehunting methods has become an imperative necessity.

This is no easy undertaking. Judging a prospect is indeed a precarious task: there is scarcely another in engineering with fewer rules to guide and more alternatives from which to choose; and scarcely another so tempting to the dreamer, nor, in actual practice, so abandoned to rules of thumb. Yet the very size of the problem makes it inviting, and there is assurance that, with the necessity realized, improved technique will rapidly follow. The orebody is not a hopeless tangle, and there is evidence that exploration can be made to rest in advance on reasons which, though concerned with hidden and intricate things, are simple and well founded.

It is in the quest for such reasons that the writer and his associates have undertaken to decipher the leached outcrops. The surface of the ground is the most accessible level of the prospect and the cheapest level on which to work; and, once the hidden ore is correlated with its leached equivalent, there is tapped a source of information hitherto but little used. At the outset of the work, it became clear that results could be best obtained through a limitation of the field. The field selected was that of the disseminated deposits of the southwestern United States, although, for purposes of perspective, the study had to be carried somewhat into aggregated deposits and into other regions of North America.

This book outlines the knowledge yielded by this study. The book offers, not a completed technique, but fragments of one, and it aspires, not only to set up rules for immediate use, but also to indicate geological and chemical studies for the further growth of the subject.

### ILLUSTRATION AND OUTLINE OF THE METHOD

A simple example of correlation between a leached outcrop and hidden ore will illustrate the general method by which information has been built up. In Tyrone, New Mexico, a district of disseminated copper ore, after a two months' study of a square mile of leached capping from which specimens were collected by a standard method of sampling, conspicuous differences in samples became apparent.¹ The nature of these differences is indicated in the following quotation from a forthcoming paper by George Tunell, Augustus Locke and others:

Three classes were discriminated definitely: (1) rock speckled with maroon dots 0.1 to 1 mm. in diameter separated by white quartz and sericite; (2) rock speckled with larger, yellowish-brown dots, separated by sericite and quartz and stained yellow in many places; (3) rock containing no iron oxide. Under the microscope these three classes are found by Tunell to be: (1) rock containing hematite, mostly in the cavities left by the sulphide, but partly as spherulites in the gangue between those cavities; (2) rock containing goethite, perhaps half in the cavities left by the sulphides, and half as halos of plates in the sericite immediately around the cavities and as circular plates and spherulites in the gangue well away from the cavities; (3) rock containing no iron oxide.

These classes of capping were correlated with: (1) ore (of a copper content about 1.5 per cent); (2) lower grade material (down to a few tenths per cent copper); (3) "waste." The characteristics favorable to copper in Tyrone are therefore concerned with the distance the iron has

<sup>&</sup>lt;sup>1</sup> Unpublished work by P. F. Boswell, H. W. Morse, and Augustus Locke.

travelled from the place of the sulphide and with the mineralogy of the precipitates of iron which were formed. In other words, samples containing the greater proportion of iron oxide in the cavities left by the sulphide and at the same time a high ratio of hematite to goethite, are those correlated with ore. Such a ratio of hematite to goethite is indicated by a maroon color as contrasted with the yellowish brown color which means a high ratio of goethite to hematite.

The degree of assurance in this separation was such that, where the rock was bare, the outlines of former orebodies existing at the horizon of the present surface could be reconstructed with details, such as cusps, re-entrants, horses of waste rock and extensions along fractures.

But it will, of course, be understood that such outlines do not coincide with those of the hidden orebodies whose positions we desire to determine. Hence it is evident that the interpretation of leached outcrop must fall into two parts, the first of which is illustrated by this Tyrone example and the second of which is an additional and different kind of problem:

- 1. The reconstruction of the sulphide formerly existing at the horizon of the present surface: which is essentially a matter of distinguishing between effects of pyrite and effects of mixtures of pyrite and copper-bearing sulphides. This part makes up the bulk of the book.
- 2. The prediction of hidden ore: which is a matter of projecting the reconstructed sulphide into the region where ore is now expected to exist. Such a projection is shown in Fig. 1, in which the surface outline of good ground drops like a shadow diagonally to the surface of the sulphide, 500 feet below. This part of the work resembles the prediction of extensions horizontally and downward from the bottom level of a mine. It will be treated in a chapter near the end of the book.

In approaching the first part, namely the task of recon-

struction, we must realize that the leached outcrop of the enriched copper deposit emerges at the surface after the following steps of change: (1) protore to ore (the replacement of older sulphide by chalcocite); (2) ore to "metore":

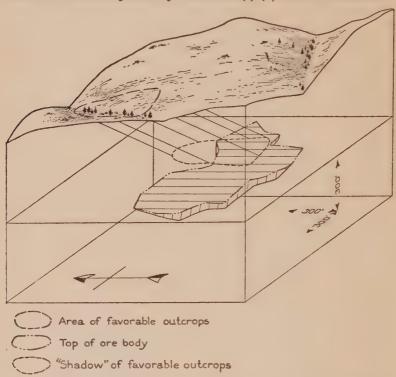


Fig. 1. Stereogram of Thistle chalcocite-pyrite disseminated orebody (Tyrone, New Mexico) showing "shadow" of favorable outcrops thrown down the structure to the top surface of the sulphide. (Area of favorable outcrops by Boswell; drawing by Tunell).

(removal of copper and sulphur); and (3) metore to outcrop (emergence of resistant parts) (fig. 2).

<sup>&</sup>lt;sup>2</sup> A term proposed to include both "capping" and "gossan," the respective oxidation products of disseminated and of aggregated ore. (See glossary.)

Of these three steps, only that of ore to metore and metore to outcrop concern us; these we must retrace by qualities found in the outcrop itself. And just as, in the past, the "circumstantial" evidence of geology has been found to yield but small result in ore discovery; so, here, such evidence must be given minor weight, and the reasoning, so far as is possible, must be based on arguments which are simple and direct. To reconstruct the sulphide will be a barren enterprise unless we know the degree of doubt involved in each of the steps leading to the conclusion.

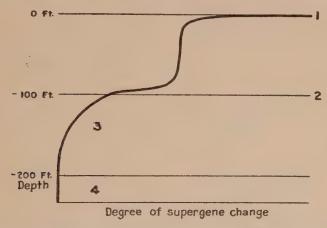


Fig. 2. Ideal diagram showing steps of change between protore and outcrop. 1, surface; 2, bottom of oxidation; 3, enriched ore; 4, protore.

With this principle in mind, we may group the kinds of evidence in the order of decreasing directness: (1) relict sulphide; (2) iron precipitate; (3) certain heavy metals in nonsulphide form; (4) porosity and oxidation collapse; and (5) gangue minerals, hypogene and supergene.

The difficulty of using these several evidences in the reconstruction of the sulphide varies directly with the ratio of sulphide to gangue. The disseminated ore capping may exactly retain former texture and volume; the iron may

remain stationary or move out into tiny halos or borders; and all the iron found in a particular specimen may have originated entirely within that specimen. But the more solid sulphide ore when it oxidizes may undergo loss or rearrangement of iron, obliteration of texture, and change of volume. The remaining gossan, shrunken and spongy, has no accordance with the sulphide and, even a quartz skeleton, through removal of iron, may collapse to quartz sand, lose all record of previous form and utterly fail in furnishing clues to the copper content of the departed ore.

The above considerations regarding the ratio of sulphide to gangue have led us to the conception of a series of metores and we have found that the place of the outcrop in this series is important in the reconstruction. At the disseminated extreme of this series, the task is simple; at the aggregated extreme, it is complicated. And within the series lies a critical point, on one side of which the iron either stays within the cavities left by the sulphide, or, being transported only within the limits of the specimen, "belongs to the specimen" and remains "within bounds;" and on the other side of which the iron is either transported beyond the limits of the specimen and is "out of bounds," or, being imported into it from an outside source, does not "belong to the specimen."

This critical point coincides roughly with the division between disseminated and aggregated ores and to the division between capping and gossan. Thus, capping shows less travel of iron than gossan does and often neither loss nor gain of iron during oxidation: in fact, for practical purposes we may assume that the iron in capping is equal in quantity to, and the iron in gossan is different in quantity from, the iron in the sulphide from which it was derived.

The series is represented by table 1 and plates I to X. The importance of the series of metores makes necessary its clear understanding early in this study.

The results found in accordance with the principles above stated will be most safely applicable in the locality where the principles have been derived. The kind of capping that

TABLE 1
Series of metores

		De	ries of i	netores				
	CAPPING OR  DISSEMINATED EXTREME				GOSSAN OR AGGREGATED EXTREME		$\rightarrow$	
Former sulphides, per cent by volume	2	5	10	15	20	30	?	?
Present "limo- nite"* or siderite, per cent by vol- ume							50	70
Fe within cavities formerly occu- pied by sulphide.	Ι	II-A V-A VII-A	III IV-A V-B	IV-B	II-B			
Fe contiguous to cavities formerly occupied by sulphide		V-A VII-A	III V-B VII-B					
Fe exported from or imported into specimen			VII-B			VIII-A	VIII-B IX	X

Roman numerals refer to plates.

means ore in one district does not necessarily mean ore in another. It is true that strong suggestions of broader rules have been found; nevertheless, the factors are so complex

<sup>\* &</sup>quot;Limonite" as used in this book is a general term including various iron precipitates. See page 105 and glossary.

that we may feel safest in our prophecies when we are working nearest to proved habits of correspondence.

Thus, kept close to the proved gradation, and used on ores not too deeply oxidized and not too complicated by variations in structure or in kinds of sulphide, the study of outcrops has developed information at low cost. And, where the rock is bare, this information has afforded a complete picture of the conditions in the horizon of the present surface. In brief, the study of outcrops improves the selection of the areas worth exporation and either challenges the advisability of further prospecting, or justifies it, and guides and economizes the operation.

### CHAPTER II

### GENERAL

### CONDITION OF PRESENT KNOWLEDGE

In the whole body of critical writings on mining geology, nothing comprehensive is directed toward leached outcrops as guides to copper ore. This means that the published knowledge of outcrops for this purpose is incidental, that it has been gathered for the sake of "completeness," and that it lacks the benefit of being tested, as part of a technique, in the field. Not being developed to meet a vital need, it cannot have escaped being plausible rather than rigorous.

The desired information, then, lies in mutually uncorrelated pieces, and, that these will fit nicely into the structure we are now undertaking, is highly improbable. What we have lacked, we realize only when some matter is critically treated. Such is the case in two recent papers by Posnjak and Merwin, which accomplished the first full characterization of "limonite" and the first correlation of different properties of hydrated iron oxides. For our purpose, these papers displaced and made obsolete writings which, though accumulating for fifty years and abundant enough to fill a book shelf, were extremely confusing.

Another recent paper, that by Butler, Loughlin and Heikes, on Utah, has information so abundant and well-considered that its authors seem to have been mindful of our particular requirements. The Zies-Allen-Mervin paper on the fundamental reactions of secondary enrichment, the Lindgren-Loughlin paper on Tintic, the Lindgren paper on Morenci, the Loughlin papers on Leadville, and the Knopf paper on Rochester, are likewise conspicuous exampler Including these, there are hardly two score writings out of

the whole geological literature which contain information directly significant for this work. But, fortunately, these summarize and select from everything which has come before and provide a real foundation, patchy but substantial. A brief review of these writings is given in the following pages.

The papers in this review, as will be seen, are overwhelmingly American. Outcrops in the great European mining districts were long since mined away and have hence been less thought of there than here. What has been actually accomplished is thoroughly presented in the paper by Schneiderhöhn.

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Blanchard, Roland, and Boswell, P. F. Notes on the oxidation products derived from chalcopyrite. *Econ. Geol.*, 20 (1925).

The only comprehensive, published correlation of particular kinds of limonite with chalcopyrite, and their contrast with the oxidation products of pyrite.

BUEHLER, H. A., AND GOTTSCHALK, V. H. Oxidation of sulphides. Econ. Geol., 5 (1910); 7 (1912).

Laboratory experiments on the oxidation of various powdered sulphides, single and in pairs, with especial reference to reciprocal acceleration and retardation effects.

The rates of oxidation and the electrical effects as determined, though suggestive, are not decisive, because of uncontrolled factors such as those of exposed surface and polarization. The studies were later carried forward by Wells and Allen.

BUTLER, B. S. Geology and ore deposits of the San Francisco and adjacent districts, Utah. U. S. Geol. Surv. Prof. Paper 80 (1913).

A paper full of significant detail from the standpoint of leached outcrops.

Butler, B. S., Loughlin, G. F., Heikes, V. C., and others. The ore deposits of Utah. U. S. Geol. Surv. Prof. Paper 111, (1920).

A source-book of fact, covering a broad range of orebodies, physiography and climate, and based on several seasons of field work.

For the study of outcrops, although most of the orebodies are aggregated rather than disseminated, it is the best single account of field conditions, and it furnishes much information which can be translated into ideas about the disseminated ores. Throughout, it carries items of interest, such as: known relations between oxidation and water level; weathering of gangue minerals, including siderite; fixation of migrant zinc as oxidized ore in limestone; occurrence of basic ferric sulphates.

Emmons, S. F. The secondary enrichment of ore deposits. Am. Inst. Min. Eng. Trans., 30 (1900).

A pioneer paper giving one of the earlier discussions of the relation of oxidation to water level.

EMMONS, W. H. Outcrops of ore bodies. Min. and Sci. Press, 99 (1909).

Contains suggestive comment, such as: composition of the outcrop by the most resistant material; chemical transportation of gold and silver; persistence of galena, enargite, magnetite, and hematite during oxidation; loss of volume during oxidation; relation of oxidation to water level.

EMMONS, W. H. The enrichment of ore deposits. U. S. Geol. Surv. Bull. 625 (1917).

A convenient compilation and review of the subject of secondary enrichment, with stimulating particulars applying to leached outcrops.

EMMONS, W. H., AND LARSEN, E. S. Geology and ore deposits of the Creede district, Colorado. U. S. Geol. Surv. Bull. 718 (1923).

Includes a discussion of the deep oxidation of thuringite, an ironrich chlorite, and the production from it of abundant "limonite."

Hoover, H. C. The superficial alteration of Western Australian ore deposits. Am. Inst. Min. Eng. Trans., 28 (1898).

Deals with the enrichment of gold in gossan and contains discussion of mechanical versus chemical agencies in enrichment.

HOOVER, H. C. Principles of mining. McGraw Hill Book Company (1909).

Contains a brief, well-balanced discussion of outcrops as guides to ore.

Hudson, A. W., and Van Arsdale, G. D. Heap leaching at Bisbee, Arizona. Am. Inst. Min. Eng. Trans., 69 (1923).

Describes a large experiment in heap leaching at Bisbee, Arizona.

JORALEMON, I. B. The Ajo Copper Mining District. Am. Inst. Min. Eng. Trans., 49 (1914).

Describes: mushrooming of primary disseminated mineralization in the intrusive under a cover now largely eroded; oxidation of ore with retention of the copper.

Knopf, Adolph. Mineral resources of the Inyo and White Mountains, California. U.S. Geol. Surv. Bull. 540 (1914).

The first clear statement of the localization of oxidized zinc ores in limestone below an oxidized galena-sphalerite deposit.

Knopf, Adolph. Geology and ore deposits of the Yerington District, Nevada. U.S. Geol. Surv. Prof. Paper 114 (1918).

Discusses the prevention of sulphide enrichment by limestone; and oxidation stopped by the impervious ore from going down to water level.

KNOFF, ADOLPH. The Candelaria Silver District, Nevada. U. S. Geol. Surv. Bull. 735 (1923).

Describes field conditions of residual enrichment in silver by removal of carbonate gangue while sulphides were being destroyed.

Knopf, Adolph. Geology and ore deposits of the Rochester District, Nevada. U. S. Geol. Surv. Bull. 762 (1924).

Describes ore made by the supergene replacement of sphalerite by argentite. The best picture of supergene, sulphide, silver enrichment.

LARSEN, E. S. The microscopic determination of the non-opaque minerals. U. S. Geol. Surv. Bull. 679 (1921).

Briefly describes the technique of, and contains the most complete set of tables for, the determination of non-opaque minerals by the method of immersed powders under the microscope. This technique is an application of the immersion liquids developed by many workers. So far as application to the iron precipitates found in outcrops is concerned, the necessary media were developed by Merwin and Larsen.

LINDGREN, WALDEMAR. The copper deposits of the Clifton-Morenci District, Arizona. U. S. Geol. Surv. Prof. Paper 43 (1905).

Like the Butler-Loughlin-Heikes paper on Utah, this paper, despite its general purpose, is a source of information about matters on which we have to fix our attention. At the time the paper was written, the importance of disseminated copper deposits was only beginning to be recognized.

LINDGREN, WALDEMAR. Mineral deposits. McGraw Hill Book Co. (1919).

Though not written with any direct interest in leached outcrops as guides to ore, this is a compilation worth repeated reading for the varied suggestions which it yields.

LINDGREN, WALDEMAR, AND LOUGHLIN, G. F. Geology and ore deposits of the Tintic Mining District, Utah. U. S. Geol. Surv. Prof. Paper 107 (1919).

Discusses: oxidation below water level; sudden drop of water level between igneous rock and limestone; occurrence of jarosite and plumbojarosite; mineralogy including the mineral absentees; replacement of kaolin by limonite on a large scale; distinction between chert independent of ore mineralization and jasperoid associated with it.

LOUGHLIN, G. F. The oxidized zinc ores of Leadville, Colo. U. S. Geol. Surv. Bull. 681 (1918).

A comprehensive treatment of oxidized zinc ores deposited in limestone below oxidized galena-sphalerite orebodies: excellent mineralogy; important in study of sulphides oxidizing in limestone.

LOUGHLIN, G. F. Zinc carbonate and related copper carbonate ores at Ophir, Utah. U. S. Geol. Surv. Bull. 690 (1919).

The deposition of oxidized zinc ores in limestone; the development of cellular texture; lead carbonate; basic copper carbonates; paragenesis of the carbonates of copper and zinc.

LOUGHLIN, G. F. Notes on ground waters. Econ. Geol., 19 (1924).

A thoughtful statement of the more modern conceptions regarding ground waters: relation between water level and oxidation.

LOUGHLIN, G. F. Guides to ore in the Leadville District, Colorada. U. S. Geol. Surv. Bull. 779 (1926).

A summary, from the forthcoming professional paper, of data and ideas bearing especially on the search for ore. Few outcrops have been visible in recent years, and the paper is concerned largely with underground guides. Yet, because those guides are applicable to the projection of surface showings into unexplored ground, the paper is important from the outcrop standpoint.

McBain, J. Oxidation of ferrous solutions by free oxygen. J. Phys. Chem., 5 (1901).

Incidentally gives disscussion of the influence of acid in the oxidation of ferrous sulphate.

Meinzer, O. E. The occurrence of ground water in the United States. U. S. Geol. Surv. Water Supply Paper 489 (1923).

A compilation of facts and discussion of principles. The statement of principles is broader than that elsewhere available and is supported by more abundant evidence. The matter on the capillary control of water movement, especially in the capillary fringe, the definition of the zone of aeration, and the evidence regarding freedom of flow in various materials and regarding control of direction of flow, are especially useful for our purpose.

MERWIN, H. E., AND LARSEN, E. S. Mixtures of amorphous sulphur and selenium as immersion media for the determination of high refractive indices with the microscope. Am. Jour. Sci., 34 (1912).

MERWIN, H. E. Media of high refraction for refractive index determinations with the microscope; also a set of permanent standard media of lower refraction. *Jour. Wash. Acad. Sci.*, 3 (1913).

These two papers provide media for the measurement of the indices of refraction of minerals exceeding 1.74 in index. This class of minerals is large and includes most of the iron precipitates found in leached outcrops. Without these tools, the investigation of these minerals, of vital importance to the outcrop study, would have been impossible.

(The tables in the second paper contain several printer's errors.)

Morse, H. W., and Locke, Augustus. Recent progress with leached ore capping. *Econ. Geol.*, 19 (1924).

Estimation, from capping evidences, of the former sulphide grade. Nishihara, G. S. The rate of reduction of acidity of descending waters and its bearing upon secondary sulphide enrichment. *Econ. Geol.*, 9 (1914).

The rates were determined for several minerals. Because of the varying factors, such as area of exposed surface, the rates can be accepted as merely suggesting, and not proving, the order between the minerals.

Posnjak, Eugen, and Merwin, H. E. (1) The hydrated ferric oxides.

Am. Jour. Sci., 47 (1919). (2) The system, Fe<sub>2</sub>O<sub>3</sub> - SO<sub>3</sub> - H<sub>2</sub>O.

Jour. Am. Chem. Soc., 44 (1922).

The first paper proves that no series of hydrated ferric oxides exists; that there is one hydrated ferric oxide, Fe<sub>2</sub>O<sub>3</sub>·H<sub>2</sub>O, occurring in two crystalline forms, goethite and lepidocrosite; and that the variation in water content of "limonite," the "amorphous" form, is due to adsorbed and capillary water.

The second paper defines the conditions of temperature and concentration under which  $\mathrm{Fe_2O_3}$ ,  $\mathrm{Fe_2O_3}\cdot\mathrm{H_2O}$ , and basic, normal, and acid ferric sulphates are stable, and gives the optical properties of the crystalline products.

These papers are of the greatest importance in outcrop study and constitute a stimulus for future field and laboratory work.

RANSOME, F. L. (1) Geology of the Globe Copper District, Ariz. U. S. Geol. Surv. Prof. Paper 12 (1903). (2) The geology and ore deposits of the Bisbee Quadrangle, Arizona. U. S. Geol. Surv. Prof. Paper 21 (1904). (3) The geology and ore deposits of Goldfield,

Nevada. U. S. Geol. Surv. Prof. Paper 66 (1909). (4) The copper deposits of Ray and Miami, Arizona. U. S. Geol. Surv. Prof. Paper 115 (1919).

Well-rounded papers with abundant observations in several of the important districts: though not directly treating leached outcrops as guides to ore, they serve as points of support for the construction of the outcrop technique.

RANSOME, F. L. Criteria of downward sulphide enrichment. Econ. Geol., 5 (1910).

A thoughtful treatment of the mineralogical, chemical and textural criteria of downward sulphide enrichment: contains suggestions useful in outcrop study.

RIDGWAY, ROBERT. Color standards and nomenclature. A. Hoen and Co., Baltimore, Md. (1912).

1115 named color patches; useful for color distinctions in out-

Sales, R. H. Superficial alteration of the Butte veins. Econ. Geol., 5 (1910).

A condensed, informing account of the Butte outcrops.

SALES, R. H. Ore deposits at Butte, Montana. Am. Inst. Min. Eng. Trans. 46 (1913).

A statement of facts accumulated through many years of work in the district: from the outcrop standpoint, the relation of oxidized material and ground water is especially interesting.

Saxén, Martti. The petrology of the Otravaara district of eastern Finland. Bull. Comm. Geol. Finlande, 65 (1923).

Describes natural borgströmite (3Fe<sub>2</sub>O<sub>3</sub>·4SO<sub>3</sub>·9H<sub>2</sub>O).

Schneiderhöhn, H. The oxidation and cementation zones of the sulphide ore deposits. Fortschritte der Mineralogie, Kristallegraphie und Petrographie, 9 (1924).

A summary of the existing knowledge. Of particular value to Americans because it gives a digest of the pertinent contributions by the work of foreign writers. Contains at various places new suggestions from the author's own broad experience, such as the following:

"Often to this day the sulphides remain undecomposed to the surface in the extremely arid Namib desert" (S. W. Africa).

The best developed secondary enrichment in S. W. Africa is in the "tropical normal arid regions with a periodic rainy season."

Spencer, A. C. The copper deposits of the Encampment District, Wyoming. U. S. Geol. Surv. Prof. Paper 25 (1904).

Describes gossans, notes coincidence between water level and bottom of thorough oxidation, and gives a general, yet striking, suggestion on the use of the surface as a guide to ore.

Spencer, A. C. The geology and ore deposits of Ely, Nevada. U. S. Geol. Surv. Prof. Paper 96 (1917).

A stimulating treatment of many questions pertinent to the study of outcrops, especially relation of oxidation to water level.

STICKNEY, A. W. The pyritic copper deposits of Kyshtim, Russia. *Econ. Geol.*, **10** (1915).

A description of a collapsed, residual, barite-quartz sand, made from the oxidation of a heavy pyritic ore.

Sullivan, E. C. The interaction between minerals and water solutions with special reference to geologic phenomena. *U. S. Geol. Surv. Bull. 312* (1907).

Experimental information on the function of gangue in preventing the leaching of metals, including copper.

Wells, R. C. Electric activity in ore deposits. U. S. Geol. Surv. Bull., 648 (1914).

An examination of the effects of electric activity on the behavior of sulphides under reducing conditions: discusses pyrite as an "unattackable electrode."

Wells, R. C. The fractional precipitation of some ore-forming compounds at moderate temperatures. U. S. Geol. Surv. Bull. 609 (1915).

Proves by experiment the order in which various metallic compounds are precipitated in the presence of each other: of interest to us in connection, for example, with the effect of carbonate gangue on the behavior of the sulphides during oxidation.

ZIES, E. G., ALLEN, E. T., AND MERWIN, H. E. Some reactions involved in secondary copper sulphide enrichment. *Econ. Geol.*, 11 (1916).

A closely connected, quantitative study which establishes the basic reactions of secondary copper sulphide enrichment. Attention should be directed to a conclusion of the paper which, though fundamental, has been repeatedly overlooked, to wit, the rôle of the cuprous ion in effecting enrichment. Cuprous sulphate is a far more active agent than cupric in the production of chalcocite. Ferrous sulphate, always present in the natural system, reduces cupric sulphate, supplied by the oxidizing sulphide higher in the deposit, to cuprous sulphate. This reduction is an equilibrium reaction:  $2\text{CuSO}_4 + 2\text{FeSO}_4 \rightleftharpoons \text{Cu}_2\text{SO}_4 + \text{Fe}_2(\text{SO}_4)_3$ ; or, in the ionic form:  $\text{Cu}^{++} + \text{Fe}^{++} \rightleftharpoons \text{Cu}^+ + \text{Fe}^{+++}$ .

This equilibrium is reached with a very small concentration of cuprous ion. If the cuprous ion is removed by precipitation of chalcocite, more will form by reaction from left to right; but in this reaction ferric ion also must form and as its concentration increases, that of cuprous ion must decrease. If, then, the ferric ion is removed, as by reaction with gangue, the production of cuprous sulphate and therefore the relatively rapid deposition of chalcocite can continue.

This paper supersedes the preceding studies. It presents numerous facts which pertain to the subject of leached outcrops, as, for example, the decomposition of various sulphides by H<sub>2</sub>SO<sub>4</sub>, and it must be understood in detail by those interested in this subject.

From the above review of the writings, it is evident that the problem of outcrops is here and there illuminated in the literature. In what immediately follows, we shall consider these same writings by subjects, indicating the portions still remaining obscure and suggesting questions needing to be answered.

The changes in the upper few feet of the metore have been given but scant attention: no criteria have been presented for distinctions between changes occurring there and changes at the top of the sulphide. For instance, while Lindgren, in Morenci (Arizona), laid an excellent foundation for such criteria by discussing the destruction of pyrite in the upper few feet, the disappearance of oxidized copper minerals somewhat deeper, and the change of garnet to limonite, this matter has never been carried forward by the geologists who succeeded him there, and it is still impossible to tell just where these changes occur.

The changes at the bottom of the metore (ore to metore) have been described many times in connection with supergene sulphide enrichment. But the chemistry, in most of the papers, is based on conventionalized "reactions," without experimental confirmation; or, if based on experiment, the experiments failed to maintain sufficient equality of exposed surfaces to yield consistent results. Impressive exceptions are the Posnjak-Merwin, the Zies-Allen-Merwin

and the Wells papers: these contain the principal published laboratory data for our use. Also important is the work of Allen who investigated the oxidation of various sulphides by FeCl<sub>3</sub>, KMnO<sub>4</sub>, H<sub>2</sub>O<sub>2</sub>, etc., taking especial care to control the surface: but this work, while showing the order of the rates, includes such discrepancies as discourage the experimenter from publishing his results. Data on the effect of acid in promoting the decomposition of the sulphides are given in Allen's work and in the Zies-Allen-Merwin paper. The effect of copper in increasing the rate of oxidation of ferrous sulphate is being investigated by Posnjak who finds it important (unpublished work). The effect of acid in hindering the oxidation of ferrous sulphate was investigated by McBain. The modifications in the system Fe<sub>2</sub>O<sub>3</sub> -SO<sub>3</sub> -H<sub>2</sub>O by the addition of the reagents common in natural oxidation, such as compounds of copper, potassium, and sodium, have not been looked into.

Indeed, the chemistry and the geology, till lately, have remained remote from each other. Such ideas as possible variations resulting from the escape of SO2 into the air are only now, through the work, on the one hand, of the Geophysical Laboratory, and, on the other hand, of such geologists as Butler, Knopf, and Loughlin, being carried into the field. Questions like this compel an attitude of interest toward the position of the water level, for the chemistry of merely moistened, aerated sulphide, in which any solution concentration is possible, must differ from that of sulphide immersed in water. But, though much has been written, there is little agreement among those best qualified to speak. The use of jarosite as an indicator of the solution concentration during oxidation; the significance of a smooth, flattish, lower boundary of oxidation; the effect of a long pause of erosion in sending oxidation below water level: the influence of channels with deep outlets in promoting the speedy descent of dissolved oxygen; the influence of limestone and copper sulphate in the precipitation of limonite below water level: these subjects are touched here and there, but only incidentally. Butler, Loughlin, and Heikes, however, give some of them a treatment that begins to meet our needs.

Kaolin, sericite, fine-grained quartz, and orthoclase are repeatedly and carefully described as companions of copper minerals: but their use in outcrops to indicate copper below has remained undeveloped. No success has been attained in determining the quantities of kaolin produced in the alterations respectively of pyrite and of chalcopyrite to chalcocite; nor has success been attained in separating that kaolin produced during sulphide enrichment from that produced during sulphide oxidation. And the whole subject of kaolin and its separation from the kaolin-like minerals is only now beginning to be comperhensively undertaken.

Porosity as an index of sulphide below; the increase in porosity with the change of massive sulphide to gossan and the consequent effect on the path followed by oxygen and surface water; the differences of result produced by fine pores and coarse pores; porosity as a prerequisite of deep sulphide enrichment; the travel of air through disseminated capping, whether as gas or dissolved in water; and whether at the rate of one foot a day or a hundred: all these are little studied. There are no general data as to whether capping and ore have 5 or 10 per cent of voids, or more, or less.

Cavities made by removal of sulphide are mentioned frequently but never with the idea of their systematic variation with the several sulphides from which they come. Special cases of cavities and collapse are given by Knopf in Candelaria (Nevada) and Stickney in Kyshtim (Russia), and a very lucid statement of the general process in Bisbee (Arizona) is made by Ransome. Though collapse during oxidation must have been large in numerous American metores, such as those of Shasta County (California).

Ducktown (Tennessee), and Jerome (Arizona), and, though it must have resulted in the concealment of certain friable metores under soil and their consequent failure to be discovered, the subject is but little developed in American literature.

The meaning in the outcrop of particular quantities of oxidized copper, lead and zinc, in terms of sulphide below, is but vaguely hinted at. Important preparation for developing this meaning, however, was accomplished by Sullivan, who found that in several days' time, at room temperature, the natural silicates precipitate the metals from solutions of salts while the bases are dissolved from the silicates in nearly equivalent quantities. Furthermore, Knopf in Cerro Gordo (California), Loughlin in Leadville (Colorado), and Butler, Loughlin and Heikes in Utah, describe precipitation of zinc by calcite or other carbonates.

Relict sulphide as indicative of sulphide below has been irregularly treated. The subject of mechanical protection has been mentioned but not systematically studied: that of protection through low reaction rate and through high electric potential is discussed by Wells and others but, excepting as regards the preservation of pyrite, its present application to natural oxidation has remained too complicated to yield practical rules. No attention has been paid to possible protection by CO<sub>2</sub> or SO<sub>2</sub> evolved during oxidation; and only one attempt (by Morse in unpublished work) has been made to study true samples of relict sulphide taken from the surface down to the ore.

The iron oxide precipitates, from our standpoint, have never been classified. Their mineralogy is difficult; only lately, with the work of Butler, Hewett, Knopf, Larsen, Loughlin, Merwin, Posnjak, and Tunell, have the distinctions begun to be critically made between hematite, goethite, and jarosite, long mapped under the general names of "limonite" and "hematite." Groups of physical quali-

ties, such as texture and color, signifying derivation from particular kinds of sulphide, have never been defined except by Blanchard and Boswell, and by them only in reference to chalcopyrite.

Even the simple grouping of the iron precipitates into those replacing sulphide and those replacing gangue or occupying open spaces has never been emphasized. And yet, as we shall see, this grouping is readily made and once made and understood it becomes significant; for the first kind suggests ore rich in copper and the other kind ore rich in pyrite.

### ACKNOWLEDGMENTS

Inadequate as the writings are, they have affected the whole conduct of the outcrop study. Moreover, the contributions derived in personal discussion of our specific questions with the authors have proved very vigorous indeed.

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E. S. Bastin, T. M. Broderick, John Johnston, E. S. Larsen, Waldemar Lindgren, R. C. Wells, and David White have contributed occasional discussion.

G. N. Bjorge, Ira Joralemon, H. M. Kingsbury, L. E. Reber, R. H. Sales, J. B. Tenney, and P. D. Wilson have contributed impressions from the standpoint of the examining engineer.

The Secondary Enrichment Investigation, made ten years ago, was the occasion of the first interest in the subject on the part of the writer. E. H. Perry (afterward killed in the war) was associated with the work and was constantly feeling his way into the interpretation of outcrops. Later,

the Investigation, through L. C. Graton, contributed the expenses of a two months' study by George Tunell in Arizona.

The actual field and laboratory work directed toward the outcrop problems has been in progress for the last six years. The following have, during that time, collaborated closely with the writer: C. H. White (1920–1922); Roland Blanchard (1921–1926); P. F. Boswell (1923–1926); George Tunell (1923–1926); Nahum Sabsay (1925–1926).

H. W. Morse has carried out laboratory experiments, and has been constantly involved in the development of ideas, especially on the chemical side.

F. L. Ransome has taken an interest in the investigation from the first and has drawn to the attention of the investigators many pertinent, additional facts.

Roland Blanchard and P. F. Boswell have spent long periods in the field and have therefore had exceptional opportunities for collecting information and verifying ideas. The form of classification into "significant kinds" of "limonite" is, in an important sense, their contribution. Furthermore, Roland Blanchard has undertaken an important part of the expense of preparing illustrations.

Nahum Sabsay has worked in the laboratory and has made, regarding the form of presentation, numerous suggestions which were used in bringing the writing to its present form.

George Tunell has contributed information and photographs from a forthcoming paper on the oxidation of disseminated copper ore at Morenci (Arizona), Bingham (Utah), and Tyrone (New Mexico). This paper gives the results of a field study of columnar sections penetrating both leached capping and enriched sulphide and of a laboratory study of samples representing those sections.

E. T. Allen has contributed the results of his unpublished experiments on the oxidation of sulphides.

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The Geophysical Laboratory has been similarly hospitable and has supplied discussion and criticism essential to the progress of the work.

To the enterprise, then, many have contributed and this book is the result of the combined efforts of many workers.

### CHAPTER III

### SAMPLING THE METORE

As was stated above, the principal task of this work is the reconstruction of the sulphide formerly existing in the plane of the surface. This reconstruction must be effected from the metore which is accessible, and must involve, as a first step, the problem of choosing a sample of that metore to work on. We are confronted by materials, hard and soft, exposed and covered, and we have to learn which to select.

It must be understood that, while the destruction of the sulphide is practically completed at the bottom of the metore, and while the metore is a material which weathers with extreme slowness, it nevertheless undergoes another striking change of composition as the surface is eroded down to it. For there it is subjected to renewed attack. conditioned by the increase of air travel and evaporation; by the surface concentration of soluble substances; by the heating effects of the sun's rays; by daily and seasonal fluctuations of temperature; by organic decomposition products: by the decomposition products of the last vestiges of sulphide; and by migrant surface waters.

We are therefore brought to the detailed scrutiny of the changes that take place in what may be termed the "surface layer." Those changes are partly chemical but chiefly mechanical and in thinking about them we must remember. above all, that the outcrop is only that part of the metore which survives the attack of the weather

# PROCESSES IMPAIRING THE VALIDITY OF THE OUTCROP AS A SAMPLE

## Residual concentration of harder parts

The most significant change in the surface layer is the emergence of hard material. This, in the form of knobs, tends to monopolize the outcrop, and fragments wasted from those knobs tend to predominate in the surrounding debris.

This hard material constitutes a false sample of the metore, for its very emergence is due to non-representative qualities. For example, in Ely (Nevada), a hill slope, abundantly armored with jasperoid, suggests jasperoid ground below. Yet tunnels show only occasional spots of such ground and prove erosion to have lingered at an especially resistant stratum.

But not only are the hard knobs a false sample of the metore; they are that part of the metore which is most difficult to reconstruct. Thus, one of the commonest emergent bodies is "jaspery limonite," a material in texture and form profoundly changed from the sulphide which preceded it.

Moreover, even should success be attained, despite these difficulties, in reconstructing from the hard knobs the sulphide from which they come, the result would tend to be lower grade than the average of the ground, since the metores of good copper sulphide tend to be less resistant and less represented than those of sulphide rich in pyrite.

Now, in this emergence of hard material, an essential step is what may be called "surface crackling" and its recognition is necessary to the understanding of other surface changes.

Surface crackling consists in the development of new cracks often following older structures, such as hypogene veinlets, yet often crosscutting them. It permits rock fragments to become wedged apart by soil.

As the crackling progresses, the soft material goes to powder and the hard material to fragments set in soil. From each eminent knob, these fragments may creep outward many feet without revolving, and thus the mantle of waste, consisting of fragments and their matrix of soil, may constitute a natural pavement, differing sharply in character from the underlying metore.

How misleading the pavement may be is illustrated in Ely (Nevada), where a mantle of waste 2 feet thick, overlying the metore of a disseminated orebody, showed in several countings about five pieces out of one hundred which would be termed "good capping;" while the metore in place below showed fifty out of one hundred.

## Surface hardening

The projecting corners and peaks of outcrops and of fragments set in soil are here and there "case-hardened" and the recognition of this result as a surface phenomenon is, of course, essential to the taking of a good sample. Its significance is vividly illustrated in an account given by H. E. Gregory with samples of sand cemented by calcite, which he brought from Australia: a railway construction crew working among hillocks was preparing to break hard rock and had provided appropriate machinery; but, once the crust was broken, they found that sand could be shovelled out and that the hillocks were merely cased sand dunes.

The effect of surface hardening on disseminated metore is well shown in Tyrone (New Mexico). Here, on the hill tops and part way down their slopes, a remarkably large proportion of the specimens have a vitreous appearance. These were at first interpreted as meaning silicification down to a horizon lying somewhat above the gulch bottoms. As the study progressed, however, this supposed silicification was found to be a merely superficial casing.

The metore in which this casing develops is of "disseminated porphyry ore" origin. It is the typical aggregate of fine-grained minerals, sericite, quartz, feldspar, and kaolin

with various amounts of "limonite," traversed by veinlets of these same minerals. The qualities found essential to the hardening effect are the possession of a fine porosity and a rather high alumina content. All the metores developing the casing adhere to the tongue and the metores lacking this quality, such as those composed of quartz or of dense "limonite," show no hardening.

The hardened material may be either a surface casing or an inner casing covered by a thin layer of whitish metore resembling that of the interior. (See plate XIII.) It develops in sun-exposed corners, thickening at the apex to glassy knobs several centimeters in diameter. It parallels the outer surface of the rock, with only small re-entrants following cracks toward the interior. At the soil line, it ceases, as though air or sunlight were needed for its production.

The hardening process consists in the plugging of the pores. While the metore itself is whitish and soft, the casing is dark, almost flinty, and does not adhere to the tongue. In some examples, Merwin found cavities lined first with hematite and jarosite, then further lined with opal and finally almost filled with chalcedony. The material stopping the pores is in part, at least, opal, chalcedony and quartz. But under the microscope there is, after all, no conspicuous difference between the casing and the rest of the metore, for the hematite and jarosite are produced lower down and only the opal and chalcedony, which are small in amount, can with any certainty be identified as surface effects. There is also a micaceous mineral of uncertain origin which Merwin found to be dissolved out of the outer unhardened skin. The casing sometimes cuts out veinlets and rings of "limonite" as though some "limonite" were unstable under the particular surface conditions here existing; and the casing itself is interrupted by veinlets of hypogene quartz.

The hardening may be conceived as a result of super-

saturation in capillary pores, and this supersaturation in turn as a result of evaporation and of temperature changes from day to night. Not only is the effect confined to sun-exposed surfaces, but it is even in some cases controlled by the duration of the sun-exposure, being thicker on the south-sloping and thinner on the north-sloping surfaces of the outcrop. Kingsbury, investigating this question in Tyrone (New Mexico), though he found on one outcrop equal casings

TABLE 2
Thickness of casing

IN KNOBS ON THE NORTH SIDE OF THE OUTCROP	OF THE OUTCROP
cm.	cm.
0.2	0.5
0.4	0.0
0.5	0.1
0.0	0.5
0.2	1.0
0.1	0.3
0.1	1.5
0.1	0.4
0.3	0.2
0.4	0.3
Гotal2.3	4.8
Average 0.23	0.48

all the way around, in another found conditions as shown in table 2.

From a third outcrop, 25 feet in diameter, Kingsbury knocked off forty knobs, and on the north side he found casings only 1 to 3 mm. thick and often entirely lacking; but on the south side he found almost every knob to be vitreous to the depth of 2 or 3 cm.

Whether or not the casing retreats inward as erosion progresses, is not known. We may be sure, however, that it is formed with sufficient speed to be governed by the relatively "new" breaks of "surface crackling" and to be well

developed in loose fragments of metore: and we find that, though these fragments have slid many feet, they have in many cases not turned over since the hardening began. Nor, in those examples in which the hardened part is an inner casing, has the outer layer, though kaolinic and pulverulent, had time to be eroded.

The process of surface hardening resembles that of "desert varnish" and the hardened specimens are, in fact, sometimes coated with "limonite" of the common, desert varnish type.

This discussion of surface hardening is necessitated by the danger of false sampling which becomes especially great because of the tendency of the geologist to take for examination the most readily accessible and, therefore, the most hardened knobs. Once recognized, however, the hardened materials are easily identified and avoided.

## Decomposition of relict sulphide

After the emergence of the hard knobs is understood and the mantle of waste is cut through, we may still fail to find materials truly representing the metore. For there are chemical decompositions that may affect the metore for several additional feet downward.

One of these decompositions is that of relict sulphide.

Just how close the relict sulphide comes to the surface before it begins to decompose, has not been well investigated. But the impression is that it survives nearly to the top and that a cut of two feet into the solid metore will find relict sulphide not less abundant than that existing farther down. For instance, in Morenci (Arizona), Lindgren says, "Some pyrite remains to the last and disappears wholly only a short distance below the surface."

# Decomposition of oxidized copper and iron minerals

Another of the decompositions in the surface layer is that of certain oxidized copper and iron minerals. Often, prospectors digging on mere stains of malachite, chrysocolla, or brochantite, find the copper minerals coming in strongly enough at the depth of a foot or two to make small bodies of oxidized shipping ore. Such conditions are sufficiently common to prove the leaching of copper in the surface layer and its accumulation a short distance below the sinking surface of erosion.

A good example of such accumulation occurs at Silverbell (Arizona), where, in several prospects, oxidized copper minerals, scattered through alaskite porphyry, are commonly leached to the depth of a few feet and there reconcentrated.

More commonly noted, however, is the leaching of copper from the surface layer with no recognized reaccumulation of copper below. Butler, referring to Utah in general, says that the relatively soluble basic sulphate of copper breaks down under near-surface conditions. Lindgren, speaking of Chuquicamata, says (oral communication) that the ore there, consisting of stringers of brochantite or other basic copper sulphate threading an altered igneous rock, is irregularly changed in the upper 10 or 15 feet, with partial loss of copper, to "limonite" and hematite and to the sulphates, jarosite, gypsum, and coquimbite.

The iron minerals in the surface layer undergo far less change than do the copper minerals. So far as we know, goethite and hematite are decomposed only to a very small extent. They might in some cases, however, attain so pulverized a state (by grinding or by liberation from a matrix such as kaolin in which they existed as stain) as to be carried away in suspension.

Jarosite, a basic ferric potassium sulphate and one of the important records of the departed sulphide, is, of course, more likely than the iron oxides to be changed in the surface layer. Hewett says (oral communication) that in certain Southern Nevada occurrences of aggregated deposits, jarosite, while abundant below, is replaced by "limonite" in the outcrop. Tunell, from the studies of his columnar sections in disseminated deposits, found the jarosite persisting at the surface in Tyrone (New Mexico), and Bingham (Utah) with extremely little alteration, and in Morenci (Arizona) with no alteration whatever. It appears that the jarosite in disseminated deposits does not undergo sufficient alteration even in the surface layer to invalidate seriously the sample.

An important fact regarding the travel of iron in the surface layer is the widespread occurrence there of an iron paint on broken surfaces. This paint, if not understood, will be misleading and its superficial character must, therefore, be recognized and its origin investigated.

The paint is best developed on quartzose metore buried in soil or recently exposed and is confined to cracks or to surfaces of separation from the soil. Almost always it is of film thickness; rarely, on overhanging surfaces, it accumulates as blisters or incipient stalactites. Baked in the sun, it becomes "desert varnish."

Kaolinic or sericitic metore, on the other hand, has less paint, because the "limonite" soaks in and disperses throughout the capillary interstices.

From this brief review of the decomposition of relict sulphide, and of oxidized copper and iron minerals in the surface layer, it is evident that copper, iron and sulphuric acid must there be liberated. The presence of ferric sulphate, for example, is implied at Silverbell (Arizona), where veinlets of oxidized copper minerals change upward to veinlets of "limonite."

In addition, though ordinary weathering in the semi-arid Southwest is of subordinate importance, and though the given alteration result in these metores is presumptively from sulphate waters, carbonic, humic and even hydrochloric acids must sometimes be effective. In Morenci (Arizona), Lindgren considers the absence of brochantite and chrysocolla from the immediate surface zone of veins

in porphyry to indicate that they have been dissolved by  $H_2SO_4$  and  $H_2CO_3$ .

Moreover, it is to be remembered that the rate of the chemical action approximately doubles with each 10°C. increase in temperature and that, therefore, the sun-exposed skin of the rock may in extreme cases attain temperatures in which the rate of chemical change would be 20 to 30 times that in the main body of the metore below.

## Weathering of rock minerals

Engineers frequently ask how much "limonite" in outcrops has been derived, not from sulphides, but from ironbearing rock minerals. This may be a problem in hot, humid climates where rock weathering goes deep, and even in dry climates if the ore is aggregated and able to liberate abundant acid during oxidation. But, fortunately, in the disseminated metores of the Southwest it is no problem at all.

Here the principal metore rock minerals are quartz, sericite, kaolin, and feldspar. Minor minerals are biotite, hornblende, pyroxene, chlorite, garnet, epidote, siderite, serpentine, hematite, and magnetite. The alteration of all these minerals does occur to some extent at the surface, but to so shallow a depth that the handpick readily cuts through into unaltered material. This does not mean that "limonite" from rock minerals is negligible in all metores but that it is produced mainly, not in the surface layer, but at the top of the sulphides, and not from disseminated but from aggregated ores. It will be treated from that standpoint in a later chapter.

#### THE SAMPLE

The considerations outlined in this chapter imply that neither the scattered knobs of emergent outcrop nor the mantle of waste derived from such knobs can be depended on to yield fair samples of metore for reconstruction of the sulphide in a piece of ground. Those samples must indeed be taken laboriously and carefully. No good engineer would accept random explorations in a bulky orebody as representative of that body. He could no more properly accept the random siliceous knobs of Ely, for example, as representative of the Ely metore. In either case, he must either take his sample on a formal pattern or adjust and interpret an unfair sample. He has constantly to remember that no mere desire to be fair can defend him from allowing the unfair specimen to grow and spread in influence far beyond its actual significance. This comes down practically to the conclusions that the outcrop must be so cut into that the effects of surface hardening and of other changes are passed through: and that the mantle of waste, if not too thick, must be systematically trenched. While, on the one hand. there will be small use in taking a careful sample unless it can be accurately interpreted, on the other hand, there will be small use in accurate interpretation unless the sample is known to exhibit the metore. The sampling must be abundant and equally representative of classes of materials very unequally exposed. For the use of leached outcrops as a guide to ore rests directly upon the valid sample.

### CHAPTER IV

## CHEMICAL CONSIDERATIONS

In sampling the metore, we have found that we must recognize the changes in the surface layer and cut through them to the unchanged metore below. With its importance recognized, a fair sample can be readily obtained. Now, in using the sample thus obtained for reconstructing the sulphide, one of the ways in which we learn what products are derived from given sulphides or mixtures of sulphides is found through knowledge of the oxidation process. Such knowledge is largely derived from chemical studies of the equilibrium relations and degrees of inertness of the minerals found in the metore. The results of these chemical studies make the subject of this chapter.

Sulphide copper ore and its gangue consist chiefly of the elements Si, Al, O, Ca, K, Na, Fe, Cu, and S. In oxidation, the Cu and S are largely lost; the K, Na and Ca are lost to a greater or less extent; O and H<sub>2</sub>O are added, and the resulting final, solid products consist chiefly of Si, Al, O, Fe, and H<sub>2</sub>O. (See table 3.)

These groups are, respectively, the constituents of two sets of solids, one of which by reaction with  $O_2$  and  $H_2O$  and by removal of dissolved substance, is derived from the other. It is our task to restore at least part of the first set (the sulphide) from the second set (the metore).

To accomplish this task, all we need is to find in these two groups some element or elements common to both and related in a known way to the quantity of copper in the sulphide. Only Si, Al, Fe and O are common to both. The O undergoes erratic changes. The Si and Al are sufficiently

permanent, but their relations to copper quantity have not been found to vary in a simple way although there is doubtless an intimate connection. How, then, does the Fe behave?

The quantity of iron in certain ores remains the same during oxidation, and, as will be shown later, in these the iron-copper ratio in the sulphide is in some degree determinable from the evidences afforded by the capping, partly through empirical studies of transitions away from the capping under investigation, and partly through experimental studies of the equilibrium relations in the systems involved. The

TABLE 3

SULPHIDE ORE AND GANGUE	METORE
Si	Si
Al ·	Al
0	О
Ca	Fe
K	$_{\mathrm{H_2O}}$
Na	
Fe	
Cu	
S	

iron minerals produced during oxidation have on this account become the center of this study of outcrops. A metore with an iron precipitate pseudomorphically replacing the sulphide has in very favorable cases been made to yield even a quantitative estimate of the copper in the ore previous to oxidation.

The natural chemical system, of course, exceeds in complication any which has been experimentally determined. It can be studied by the separate investigation of numerous included systems such as Fe<sub>2</sub>O<sub>3</sub>-FeO-SO<sub>3</sub>-H<sub>2</sub>O, Fe<sub>2</sub>O<sub>3</sub>-K<sub>2</sub>O-SO<sub>3</sub>-H<sub>2</sub>O and F<sub>2</sub>O<sub>3</sub>-CuO-SO<sub>3</sub>-H<sub>2</sub>O. Yet, even with these systems determined, there might be further

natural complications whose effects would have to be taken into account. For instance, variable amounts of sulphur may be withdrawn as gaseous sulphur dioxide. The supply of oxygen and the area of the oxidizing sulphide are unpredictable variables, with which the relation between the rates of oxidation by oxygen and of reduction by pyrite or other sulphide will also vary. However, the supposed complications that arise from incomplete oxidation, namely, the presence of ferrous ions in the solution and the escape of sulphur as dioxide, seem unlikely to be important in disseminated ores; for, in such ores, thorough oxidation may be assumed as a reasonable postulate.

Another complication is introduced by a lag in the achievement of equilibrium which may prevent the expected solid from appearing, or may cause a solid, once precipitated, to survive exposure to conditions under which it is unstable. On the other hand, if the reaction proceeds very slowly, the system may be in equilibrium at all times, although large changes in the concentration and mass of the solution and in the masses of the solid phases may take place.

Altogether there is reason to hope that, with the systems including K<sub>2</sub>O and CuO determined, the other complications would prove to have minor effect in the case in which we are particularly interested. Let us examine, then, the ideas justified by the chemical information already available.

The chemical considerations will be focussed on the behavior of iron during the oxidation of sulphide. In this behavior have been found two significant alternatives, the iron either staying in the place of the sulphide or being taken away from that place. It has been found, furthermore, that this difference accords with a difference in the composition of the sulphide and this gives us the kind of correlation which we need. It has developed, therefore, that our principal interest in the chemistry comes down to the question of why the iron of one sulphide travels while that of another

remains in place; or to the question, in other words, of the migration of iron.

#### PRINCIPLES OF THE MIGRATION OF IRON

It will be easier to gain an understanding of these principles if we first examine the chemistry of sulphide oxidation without admixture of gangue. This oxidation may be conveniently viewed as occurring in the following steps: (a) solution of the iron sulphides; (b) oxidation of ferrous to ferric iron; (c) precipitation of the persistent solids, goethite, hematite, borgströmite, jarosite (the double salt), and other basic sulphates.

The first step, the solution of the iron sulphides, need not be discussed, for it has so far furnished no suggestions which promise to aid us.

The second step, the oxidation of ferrous to ferric iron, has, on the other hand, become significant in the general case. Two rules have proved of especial importance. They are:

- 1. Oxidation of ferrous to ferric iron is retarded by free acid. To be more precise: If a solution approaches neutrality, the rate of oxidation of FeSO<sub>4</sub> to Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> becomes greater because of the removal from the solution of the oxidation products due to hydrolysis. Other things being equal, therefore, pyrite, whose oxidation yields free sulphuric acid, tends to have its iron remain ferrous, and therefore to be carried away, while bornite, whose oxidation produces less sulphuric acid, or none at all, tends to have its ferrous iron oxidized and thus precipitated in place through hydrolysis.
- 2. The oxidation of ferrous to ferric iron is accelerated by copper. For this reason, again pyrite tends more strongly than bornite to have its iron carried away.

The third step is subject to these same rules, for, under equilibrium conditions, the precipitation of the iron

mineral from the ferric solution is decreased by acid and increased by copper. There exists, therefore, on the basis of chemical facts, a double reason (in the general case) why pyrite should be more likely to have its iron carried away than bornite or other copper-bearing sulphide.

# EXPERIMENTAL BASIS FOR THE PRINCIPLES OF THE MIGRATION OF IRON

These principles have been based on laboratory data. Because, however, the experiments, while in some cases complete are in others merely qualitative, their discussion becomes necessary in order that the degree of assurance may be understood.

Regarding the oxidation of ferrous to ferric iron, it is known that the complete change  $Fe'' \rightarrow Fe'''$  requires a strong oxidizer such as potassium permanganate. With air oxidation, some Fe'' usually survives. This is found true not only in the laboratory products but also in the natural metores with which we have to deal; for even in gossans which, being coarsely porous, favor an excess of oxygen, Posnjak and Merwin find small amounts of ferrous iron, probably in the form of siderite. It is only in the disseminated ores that it appears probable that the amount of ferrous iron present, when precipitation of the oxidation products is complete, is negligible.

The effect of acid in retarding the oxidation of ferrous iron has been long known but has not been well measured. According to McBain, the rate of oxidation of ferrous sulphate is proportional to the concentration of the oxygen and roughly to the square of the concentration of the ferrous iron. Addition of free acid retards the oxidation but in no case does the retarding effect reach direct proportionality to the concentration of the free acid. He, and later Morse, illustrated the effect of acid by blowing air for several days through an acidified FeSO<sub>4</sub> solution at room tempera-

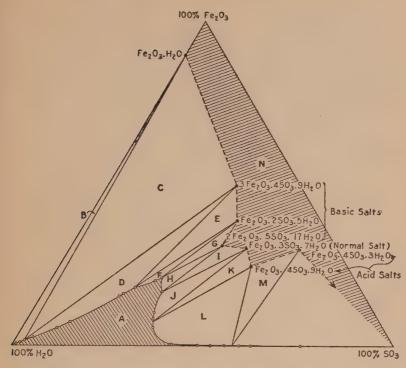


Fig. 3. The Posnjak-Merwin 50° isotherm. A, area in which all constituents are in solution; N, area in which all constituents are solid; B to M, areas in which particular solid compounds are stable in solutions whose compositions are indicated by points on the saturation curve bounding area A. The areas are further characterized as follows: A system of total composition corresponding to any given point within the triangles, C, E, G, I, K, and M, would produce a mixture of crystals having the compositions indicated by the upper two vertices, leaving a liquid of composition corresponding to the third vertex (which lies on the saturation curve). A system of total composition corresponding to any given point within the areas B, D, F, H, J, and L, would produce a single kind of crystal having the composition indicated by the upper vertex, leaving a liquid of composition corresponding to the point in which the saturation curve is intersected by a straight line through the upper vertex and the point representing the total composition of the system.

ture; even then, the concentration of ferric iron was barely measurable.

The effect of copper in accelerating the oxidation of ferrous iron was noted by Wells who, from his experiments with carbonates in fractional precipitation, came to the

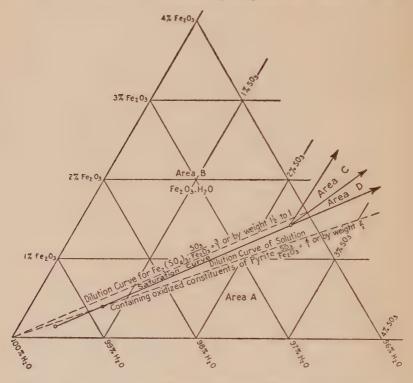


Fig. 4. Enlarged corner of Posnjak-Merwin 50° isotherm with dilution curves for Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> and for the oxidized constituents of FeS<sub>2</sub>.

following conclusion: "The presence of cupric sulphate greatly intensifies the tendency of ferrous salts to oxidize." Morse has found the decomposition of siderite, and the oxidation of the ferrous iron thus formed, to be markedly increased in speed by copper in solution. Posniak, in experi-

ments still in progress, has found that the rate of oxidation of ferrous iron is increased by copper in solution many times over.

The effect of acid in decreasing or preventing the precipitation of the persistent iron solids, and that of dilution in increasing it (both under equilibrium conditions), are treated comprehensively in the work of Posnjak and Merwin. This work defines the conditions of stability for various ferric precipitates, yielding information of the utmost consequence to the subject of outcrops, and must be understood by readers seriously interested in that subject.

The Posnjak-Merwin diagram of the Fe<sub>2</sub>O<sub>3</sub> – SO<sub>3</sub> – H<sub>2</sub>O system at 50° is reproduced in figure 3. Broadly, the purpose of the diagram is to show in condensed form what products we shall encounter with given conditions; or, given the products, what the conditions may have been when these were being formed. Among other things, it shows the conditions of formation of basic ferric sulphates and goethite. It shows that borgströmite (3Fe<sub>2</sub>O<sub>3</sub>·4SO<sub>3</sub>·9H<sub>2</sub>O, a salt which resembles jarosite, both chemically and physically, very closely) can precipitate from a solution having a minimum concentration about 1.44 per cent Fe<sub>2</sub>O<sub>3</sub>, 2.30 per cent SO<sub>3</sub> and 96.26 per cent H<sub>2</sub>O; and that, as this solution is diluted, goethite can appear. It shows that borgströmite and goethite can precipitate in succession, each over a broad range of concentration.

It shows, furthermore, that a solution containing the oxidized constituents of pyrite, in which the ratio  $\frac{SO_3}{Fe_2O_3}$  =

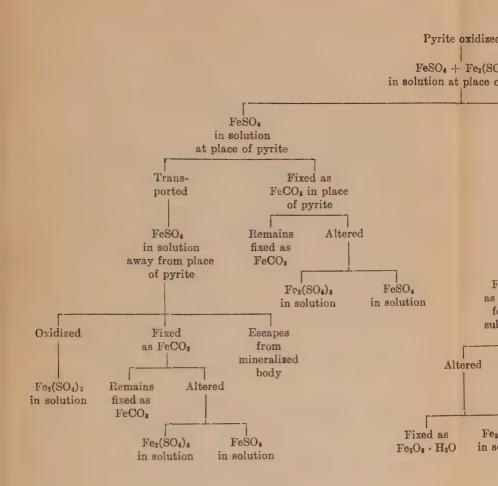
†, begins to drop goethite when the water content of the solution reaches about 98.8 per cent; hence, by dilution to that point, goethite can come out of a solution derived from the oxidation of pyrite.

Finally, if we look at the saturation curve of this diagram, we find that, as it approaches the H<sub>2</sub>O corner, its ratio

 $SO_3$  increases slowly up to a water content of about  $Fe_2O_3$  increases slowly up to a water content of about 97.5 per cent; thenceforward that ratio increases more and more rapidly, reaching and surpassing any given value. If, then, the solution be only dilute enough, goethite may precipitate despite a high ratio of acid to base. On the other hand, if the solution in which the oxidized constituents of pyrite occur has less than 98.8 per cent water, iron will not precipitate in the form of goethite replacing the pyrite, unless other components than  $Fe_2O_3 - SO_3 - H_2O$  are present in a form which will use up  $SO_3$ .

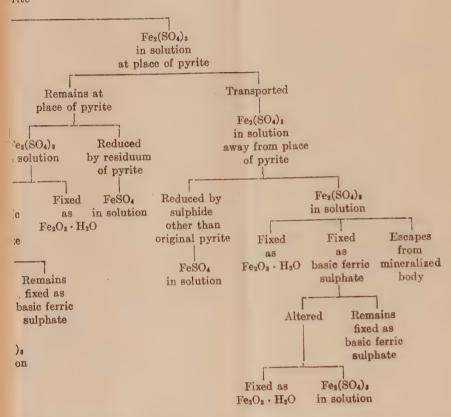
The effect of copper is not definitely known, for the system Fe<sub>2</sub>O<sub>3</sub>-CuO-SO<sub>3</sub>-H<sub>2</sub>O has not been investigated. However, Posnjak (oral communication) thinks it probable from his experience with copper and iron salts in solution, that if, to an Fe<sub>2</sub>O<sub>3</sub>-SO<sub>3</sub>-H<sub>2</sub>O solution just saturated with Fe<sub>2</sub>O<sub>3</sub>·H<sub>2</sub>O or 3Fe<sub>2</sub>O<sub>3</sub>·4SO<sub>3</sub>·9H<sub>2</sub>O, CuO is added, then Fe<sub>2</sub>O<sub>3</sub>·H<sub>2</sub>O or 3Fe<sub>2</sub>O<sub>3</sub>·4SO<sub>3</sub>·9H<sub>2</sub>O will precipitate. This means that copper would increase hydrolysis of the iron compounds and precipitation of the iron solids.

The experimental evidence, therefore, suggests that bornite and chalcopyrite or mixtures of these with chalcocite and of chalcocite with pyrite tend, with a given solution concentration, to yield more iron precipitates in the place of the sulphide than does pyrite alone.



## DIAGRAM SHOWING THE OBVIOUS ALTER

Note: The expression of oxidation products in solution as FeSO<sub>4</sub> and Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> is intersalts, but that they contain ferrous, ferric, and sulphate ions.



VES IN THE OXIDATION OF PYRITE

to indicate, not that the solutions contain constituents in the proportions of these

## CHAPTER V

# CHEMICAL CONDITIONS ABOVE AND BELOW WATER LEVEL

In the last chapter was summarized chemical information in some degree defining the behavior of sulphide iron during oxidation, yet permitting various alternatives of result. Thus, were the solution dilute, all the iron of pyrite could be precipitated as pseudomorphic "limonite." Were it concentrated, all the iron could depart, leaving a void.

The present chapter undertakes to define that behavior further by field deductions on the relation of oxidation to water level. While oxidation is in progress there is a sharp difference of condition between sulphide flooded with circulating water under hydrostatic pressure and sulphide aerated and merely moistened with water held by molecular forces. We are under the necessity, then, of learning to what extent oxidation occurs in aerated and to what extent in flooded rock.

In this subject, much has been taken for granted. Yet, at a point vital to our inquiry, the relation between water level and bottom of metore, there is a surprising amount of controversy; and we are forced for that reason to look into the whole matter. We shall start by examining the shape, attitude and sharpness of the metore-sulphide boundary.

#### THE METORE-SULPHIDE BOUNDARY

The boundary between metore and sulphide differs from one orebody to another: it may be smooth and flattish; or peaked and deeply indented; with the transition grading through a layer, varying from one to 25 feet thick, of mixed

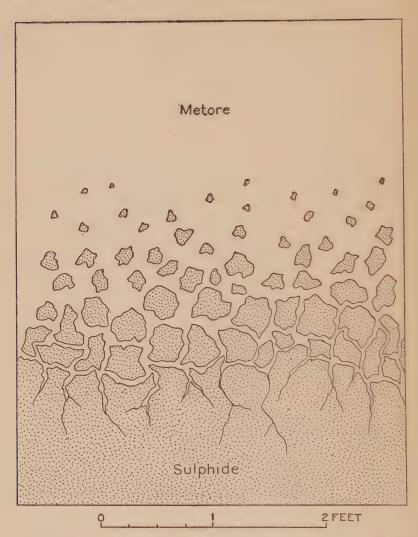


Fig. 5. Sketch of boundary between metore and sulphide at Clay orebody (Morenci, Arizona). Though there is a transition zone 3 feet thick, in which both oxidized and sulphide minerals exist, the sulphides occur there in residual, unoxidized areas having boundaries which are microscopically sharp. (Tunell.)

sulphide and metore; and, in places, with transition grading through a layer of oxidized copper ore.

All of these, and several combinations of them, are found in disseminated ore deposits. There is one combination, however, having more simple relations than the others, namely, the sudden change of sulphide to metore along a smooth, flattish surface. Such a combination is found in Ajo (Arizona), Ray (Arizona), and in a number of other districts. This we shall term "the simple case" and shall use as the starting point of discussion.

The conditions determining "the simple case" are found where the ore is widely and uniformly porous; or where it has long rested undisturbed by structural changes. Sometimes, as at Ajo, where the hills rise from a rock floor, the smooth flattish surface is extensive and coincident with the water level. Elsewhere, by artificial drainage, the water may have been lowered; or faulting or changes in water supply may have lately lowered or raised it. And, in some of these cases, as at Miami (Arizona), the smooth flattish surface persists merely in fragments, separated by faults and eaten into by later oxidation.

Now, what conditions of oxidation do the sharpness, smoothness, and flatness of this surface connote?

The surface corresponds to no original structure, causing contrasts in permeability, for the material is often homogeneous. It must, therefore, coincide with a difference in distribution, within that homogeneous material, of the weathering agents, oxygen and water.

That difference in distribution cannot correspond to a boundary between two gases, fresh air above and depleted air below; nor to a boundary between two solutions, oxidizing above and non-oxidizing below: for in those cases the surface would be gradational, or peaked, or both.

The remaining alternative is the coincidence of this surface with the boundary between air and water—the water

level itself—separating rock below saturated with water, from similar rock above with its major openings emptied of water and filled with air.

Indeed, the surface of the water is sometimes found exactly to coincide with the top of the sulphide, and, though often not coinciding, is similar in shape and attitude. These both form sudden discontinuities and they are the only such discontinuities which exist. That the water level and the metore-sulphide boundary are causally interconnected is, therefore, a conclusion impossible to escape.

These considerations regarding the simple case are associated with the question of whether the great bodies of supergene chalcocite, such as that of Miami, were produced above water level or below. As is well known, chalcocite ore bodies often fray out gradually at the bottom, at last gathering into stringers which strike downward hundreds of feet below the present or the inferred former water level. And, inasmuch as an unmarked and unperceived transition such as this, traversing the discontinuity between saturated and aerated rock, is inconceivable; and inasmuch as the chalcocite produced above water level could not avoid having inmixed "limonite;" the only conclusion is that the chalcocite was made in saturated ground and that its junction with the metore above coincided with the water level.

In the simple case, therefore, we are drawn to the hypothesis that the condition fixing the bottom of the metore can be nothing else whan the water level itself. In a given ore-body, presumption will powerfully favor this hypothesis; only where it is proved incongruous with field evidence may some other be substituted.

In "the complicated case," the metore-sulphide boundary has either an irregular shape, a graded transition, or both. This may result from instability in the water level, a condition usual in the Great Basin region where the various independent basins are alternately drained off and filled up. Or it may result from non-homogeneity in the rock, as where the water is so heaped up in bodies of clay-like material, and so depressed in adjacent bodies having large openalis, as to show no semblance of a level; and the level detere heed by the abundant entrance of water into mine workhe is may underlie spongy bodies releasing their water in a secundary with the oxidation in the more coarsely porous materials has swept down past them.

These effects are well illustrated at Majuba Hill (Nevada), where a bleb of soft clay 100 feet in diameter, lying high up near the peak of the hill which is 1000 feet high, remains moist and abundantly specked with pyrite, although the rest of the hill is dry and oxidized to its base. They are illustrated also in the Ray (Arizona) belt of disseminated copper ore. Here the water level was measured several times during the drilling of each churn drill hole; in some cases after the ground water had apparently been penetrated, the hole went dry because it cut a dam; often the water was highest when the hole was deepest; sometimes it descended as the hole deepened; now and then it suddenly ascended; and the extremes of level within a single hole were 200 feet. The Ray water level is unquestionably subject to seasonal and other fluctuation. As recorded, it seems to represent points taken at random along curves of fluctuation.

Butler describes the influence of non-homogeneity in Utah as follows: "Usually a single vein or fissure does not extend for a great distance and the height of the water table in a single vein is dependent on the permeability of the rock in which it occurs." An effect of similar nature is shown also in Butte (Montana), where veins are oxidized down to the bottom of a great sink of aerated ground having thorough rock alteration, but carry sulphides close up to the surface farther out where the granite is fresher and tighter.

The most marked effect of non-homogeneity is afforded

when porosity develops during oxidation more readily in one rock-than in another lying alongside. This phenomenon is show-than in another lying alongside. This phenomenon is show-than the aggregated deposits of Tintic (Utah) and Ely (Nevaled, where, while oxidation and water level lie many hundred of feet deep in the mineralized limestone, in the adjacentageneous rocks, they are far closer to the surface and in places even within 25 feet of it. We may say that, generally, in limestone containing or lying close to sulphide, oxida-

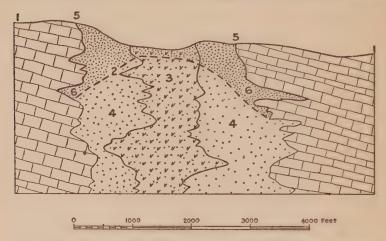


Fig. 6. Deep oxidation at junction of pyritized jasperoid with limestone. 1, surface; 2, bottom of oxidation; 3, pyritized porphyry; 4, pyritized jasperoid halo replacing limestone; 5, "limestone wall" carrying caves down to bottom of oxidation; 6, deep oxidation "sink" or "trough" at "limestone wall."

tion eats its way downward by creating caves, and tends to produce not only deep metore but also deep water level: in short, the oxidation itself forms deep drainage conduits.

In the complicated case, then, the boundary between metore and sulphide lacks the smooth, flattish character and suddenness of transition which would prove coincidence with water level. The complications are too numerous to compel such a simple conclusion. Yet, merely because the direct proof is not available, we do not therefore have to believe that a body of metore with a ragged lower boundary differed essentially in its conditions of origin from a body of similar metore having a smooth lower boundary. We have seen that the present water level, measured at a temporary stage and, indeed, even at the time of measurement only partially marking the surface between saturated and aerated material, is not necessarily a significant feature. Even in the complicated case, then, presumption favors the idea that the critical fact determining the oxidation was the position of the surface lying between aerated and saturated material at the time of oxidation.

#### OXIDATION BELOW WATER LEVEL

We have concluded that, in the simple case, the metoresulphide surface is fixed by and coincides with the surface between aerated and saturated rock. We have concluded, also, that in the complicated case, although the direct evidence is inconclusive, the first explanation to be applied is the same as that of the simple case.

We shall now examine these matters in greater detail, bringing out the contrasts between those oxidation effects proved to occur below water level and those proved to occur above.

In regard to oxidation below water level, there is a widespread opinion among geologists that rocks and sulphides there are protected from weathering alteration. Finding thorough oxidation below water level, we assume that level to have risen and we accept oxidation below it only on weighty evidence and as a last resort. For example, Butler in the paper on Utah says: "In some of the deposits in the lower ranges, the ores are oxidized considerably below the present water level and it seems not unlikely that the alteration occurred while the water in the basins was lower than at present and probably before the sediments had accumulated in the basins to the present levels."

But, though the cases of oxidation above water level are the most numerous, it is recognised that there are also unquestioned cases of oxidation below it. No reason exists why this should not be so. The whole problem is one of the relative rates at which oxygen is supplied and used up. In the simple case, oxygen is supplied to the aerated ground in overwhelming excess and to the submerged ground so slowly that it is consumed within a few millimeters of penetration. In the cases now to be considered, either the supply of oxygen to the submerged ground is more rapid, as when water with dissolved oxygen runs down a crack, or, its consumption is slower, as when the water level stands long in one place with little exposure of new sulphide.

The oxygen is supplied to the submerged sulphide in two principal forms—as dissolved gas and as ferric sulphate. From the standpoint of supply, the problems of the two forms are similar and may be considered together.

The oxygen comes into the submerged sulphide by circulation and diffusion. Diffusion, except for distances of a few feet, is slow: oxygen introduced at one end of a 100-foot water column would, by diffusion, reach measurable concentration at the other end only after thousands of years. Circulation, on the other hand, is relatively rapid: the addition of water to saturated ground from above may depress a given drop within that ground 100 feet in a few years, or even in a few hours, should that drop lie in a continuous crack. We may say that, in general, the bottom of oxidation tends to coincide with the top of the saturated ground and to be rather flat until it comes to a zone of fractures, when it suddenly sends long tails of oxidation far down below the water level. Like the dispersion of a drop of ink in a tub of circulating water, therefore, a given oxidation effect below water level must be assigned rather to circulation than to diffusion. The field evidence strongly affirms this conclusion; for sub-water level alterations are proved to occur only where there is coarse porosity, permitting ready circulation; and, with the exception of borders a foot or two wide through which diffusion is relatively rapid, neither oxidation nor chalcocite enrichment occurs in wet, clay-like bodies.

Now, admitting the general fact of alteration below water level, we shall proceed to consider the oxidation of pyrite, the sulphide whose behavior is the best understood. The cases to be examined are: sub-water level oxidation of pyrite (1) in a quartz gangue, (2) in a limestone gangue, (3) in a feldspar gangue, and (4) with the added differences produced by the presence of copper.

- 1. In a quartz gangue, the sub-water level oxidation of pyrite proceeds without interference by the gangue and stops with the formation of FeSO<sub>4</sub> and H<sub>2</sub>SO<sub>4</sub>. The iron moves out and leaves a residuum of quartz (a quartz sponge or quartz sand).
- 2. In a limestone gangue, the acid is neutralized. Oxidation can go forward to Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> and of this can be formed iron precipitates. Such precipitates made below water level, following channels, will of necessity have ragged lower boundaries like those of chalcocite.
- 3. In a feldspar gangue, the acid is less rapidly neutralized: field evidence indicates that precipitation of the iron minerals in such gangue is less usual than in calcite. But the inter-relations between rate of circulation, rate of pyrite oxidation and rate of reaction with feldspar are so complicated as to make the prediction of results in a given orebody impossible.
- 4. With copper present in solution, the probability that "limonite" will be made below water level increases. This conclusion is indicated by the Posnjak experiments (p. 40) and the process is suggested by the following equilibrium

which has already been discussed on page 16 in connection with the paper by Zies, Allen, and Merwin:

$$2 \text{ FeSO}_4 + 2 \text{ CuSO}_4 \rightleftharpoons \text{Fe}_2(\text{SO}_4)_8 + \text{Cu}_2\text{SO}_4$$

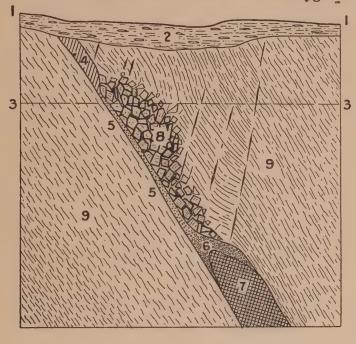
This equilibrium (to repeat what was said before) is known to be reached with a very small concentration of Cu<sub>2</sub>SO<sub>4</sub>. If, however, the acid yielded is removed, as by calcite, and if the Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> is hydrolysed to "limonite," precipitation of "limonite" can continue. Whether or not some of the large bodies of "limonite" in limestone have been made in this way is not known.

These ideas on the sub-water level oxidation of pyrite may be summarized as follows: a stable water level and a structure permitting rapid descent of solution into the saturated sulphide promote sub-water level oxidation. Under these conditions, inert gangue favors leaching of iron, while limestone gangue, or copper in solution, favors its precipitation.

The contrasts of effect between oxidation above water level and that below are especially well illustrated in the Kyshtim orebodies of the Urals (described in a paper by Stickney and orally by Kingsbury). Here, widely distributed, massive sulphide veins lying in schist and consisting of about 90 per cent pyrite and chalcopyrite with minor sphalerite, and 10 per cent quartz and barite, above water level make a porous gossan not much thinner than the sulphide; but for 50 to 135 feet from the water level downward the sulphide is removed. This removal left so fragile a skeleton of gangue that the walls collapsed. The destruction of the sulphides above the water level, on the other hand, being attended by deposition of abundant rigid "limonite," resulted in little shrinkage. In producing such contrasted effects, the relative abundance of oxygen above water level must have been of great importance.

The removal of sulphide below water level in this case

seems to be concerned with the following peculiar conditions: the physiography suggests that the water level has long stood at about its present position and that, therefore, there has been a long time in which dissolved oxygen could



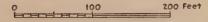


Fig. 7. Vein in Kyshtim, Russia, showing shrinkage and collapse of vein by oxidation. (Stickney and Kingsbury.) 1, surface; 2, detritus; 3, water level in vein; 4, gossan; 5, barite sand; 6, impoverished sandy pyrite; 7, massive pyrite and chalcopyrite; 8, collapsed ground; 9, schist.

penetrate the sulphide; and the abundance of pyrite and the absence of neutralizing gangue were conditions tending to make the solutions highly acid, to retard therefore the oxidation of ferrous to ferric sulphate and thus to prevent its

precipitation in stable ferric compounds. Had the walls been limestone, the sub-water level collapse of the vein could scarcely have occurred.

Ferrous sulphate encountering limestone may make siderite. Whether in a given case to expect siderite, or "limonite," or a cave in the limestone, is difficult to decide. But at times it seems to us that the siderite bodies are produced mostly in saturated and the "limonite" bodies in aerated material. In some cases, according to the reasoning on page 40, the presence of copper would make the difference between siderite and "limonite."

Siderite made by the reaction of ferrous sulphate with limestone is especially well developed in Bisbee (Arizona), where it occurs in large bodies under oxidized ground and points upward toward ore. This siderite is similar in appearance to the well-known zinc carbonate orebodies of Leadville and elsewhere and was formed in a similar way.

Another sub-water level effect when the iron remains in the ferrous state is the decomposition of the sulphide by acid. The sulphides especially attacked are pyrrhotite and iron-rich sphalerite (Zies, Allen and Merwin). With an inert gangue in which acid can persist, pyrrhotite and iron-rich sphalerite may disappear, leaving a gangue honeycombed or sandy. The result is therefore similar to that produced by the removal of pyrite but it should be remembered that, while acid alone can remove pyrrhotite or sphalerite, dissolved oxygen or ferric sulphate is required to remove pyrite.

These, however, are not the only sulphides decomposed by acid. Galena and bornite are also attacked (Zies, Allen and Merwin), but they are usually replaced by stable pseudomorphs, in the former case, of anglesite, cerrusite, covellite, or chalcocite, and in the latter case, of chalcopyrite, covellite, or chalcocite. Indeed, the most conspicuous subwater level effect is the replacement of these and other sulphides by these copper sulphides.

As we have inferred in the preceding pages, a significant condition of sub-water level oxidation is its occurrence in a bath of circulating water under hydrostatic pressure. solutions making this bath are notable for their uniformity in temperature and concentration. From season to season and from place to place within the mineral body, no sudden or great variation in either is probable. And, inasmuch as mine waters and ground waters as analyzed do not usually exceed 0.2 per cent of dissolved matter, the expectation is that the solutions were dilute and that the precipitates from them would be only of the kind which are stable in such For example, as a result of sub-water level oxidation, jarosite, or any other basic ferric sulphate, would be less probable than goethite. This is in contrast to oxidation in aerated material, where, with its mixture of air and water occurring in numerous tiny, separated capillaries or films, departures from the average concentration and temperature are certain.

It was stated above that sub-water level decomposition of sulphides is a problem of the relative rates at which oxygen is supplied and used up. It was stated further that the usual case is that of oxidation ceasing downward at flooded rock and that sub-water level decomposition means either a more abundant supply of oxygen in solution, as down a steep crack, or its slower consumption, as when the water level is nearly stationary for a long time and is therefore exposing new sulphide but slowly. Now, air tends to circulate freely as far down as the water level. Whether or not, then, oxidation will stop at water level depends on the rate at which the water level declines. This, in turn, depends both on magnitude of rainfall and on speed of erosion.

With the same rainfall and porosity, we could, then, expect critical rates of erosion: (1) so fast that oxidation would be unable to keep pace with it, as in Morenci (Arizona); (2) so slow that oxidation would outdistance it, as in Kyshtim

(Urals); and (3) such that oxidation would extend to water level but not below: the last rate is so broad in range as to make the common case.

It would be expected, then, that imperviousness and rapid cutting would promote the stranding of the metore; that great age of topography and steep open channels extending below water level would promote sub-water level oxidation; and that a uniform porosity such as that of disseminated ores, together with rather slow erosion, would promote coincidence of the sulphide-metore surface with the water level. That this last often occurs in regions having the unincised, rock floors such as those described by McGee, Lawson, Paige, and Bryan in Sonora and the Southwest, is in accordance with these ideas.

### OXIDATION ABOVE WATER LEVEL

Although oxidation proceeds in some degree below water level, it is clear that the major part of the metores in which we are interested are produced above water level.

Here, in the simple case, the water settles down through intercommunicating, coarse openings to a smooth, flattish surface. Above that surface, the blocks between these openings may still carry water in capillary pores and may supply that water in a slow drip even during a dry season. But the coarser openings are quickly emptied of water and filled with air.

The air, less viscous than the water, can readily move through these openings. Circulation is promoted by percolation of rain water, by changes of barometric pressure, by wind pressure, by in-sucking and exhalation with fluctuations in the water level, by temperature changes at the top and bottom of the metore, and by chemical combination of the oxygen. Gossans and even cappings are so porous that oxygen may be constantly renewed in all parts. With 5 per cent of intercommunicating voids, an air travel of 10

feet per day would supply 100 times the oxygen needed for the oxidation of fresh disseminated sulphide ore exposed each year by the sinking of the water level a distance of one inch.

In a sense, oxidation "eats its way," for metores are more porous than sulphide ores. For instance, though massive sulphides are not porous, their gossan is so riddled with voids that mine workings within it sometimes have a natural renewal of fresh air. Between gossan and aggregated sulphide, the contrast in porosity may be so great that water which has fallen vertically through gossan makes off horizontally along the sulphide surface.

Between disseminated sulphide ore and capping, there is no such contrast. Yet the ore, porous to begin with, is often doubled in porosity in its change to metore; it, as well as the gossan, carries abundant enlarged cracks and pores lined with hard "limonite."

From the standpoint of oxygen supply, therefore, the sulphide would be scarcely more favorably placed if it lay at the surface, and one of the reasons why oxidation in the semi-arid Southwest goes so deep is that oxidation increases the porosity and permits the water level to subside toward a deep outlet.

In the simple case, then, the bulk of the oxidation is believed to occur just above water level, and the mechanism of oxidation to proceed as follows:

The ground water settles a little; new sulphide is encountered; and the rock in the capillary fringe (Meinzer) up to a maximum height of several feet above water level remains moist though the larger openings retain only films of water and become filled with circulating air. Whether the sulphide lies in a capillary matrix or juts out into an air-filled crack, it is separated from air by water perhaps the length of a capillary tube, or perhaps only the thickness of a film of water adhering to its surface (Spencer). Oxygen

diffuses toward the sulphide, traversing lesser thicknesses of water such as a centimeter, at disproportionately greater speed than greater thicknesses such as a meter. The water becomes a solution of ferrous and ferric sulphate, cupric sulphate and sulphuric acid, which build up in concentration and diffuse outward toward the air. And in this way materials with cracks spaced 10 or 20 cm. apart oxidize readily down to water level although the inter-crack blocks may be kaolinic and have only sub-capillary openings.

The air, in addition to its oxidizing function, may have an important function of evaporation. It may be sufficiently dry (i.e., it may be circulating rapidly enough) to evaporate the solution and precipitate even the highly soluble ferrous and ferric sulphates. Through capillary openings several feet long, it may draw water toward the cracks and bring it even from the ground water. Furthermore, in limestone country, liberated CO<sub>2</sub> might be thought to have important effects in evaporation or crowding oxygen away from the sulphide, and to permit the simultaneous precipitation of chalcocite as an inner and of "limonite" as an outer layer. But, its volume compared with that of the circulating air must be small and its effect cannot be important except where, as in clay, the circulation is hindered.

However arid the air, it is unlikely to dry up adhering films of solution; for, as concentration rises, vapor pressure falls and eventually a concentration is reached at which, with a given humidity, evaporation will not proceed. Just as droplets of sulphuric acid will survive in the driest air, a film of solution will persist from one wet season to another.

Some of the products of evaporation, such as the normal salt, coquimbite (Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·7H<sub>2</sub>O), are so readily dissolved that, however abundant they might have been during their temporary existence, they would be expected to be rare in metores. Such products have been actually found in small amounts above aggregated ores; they have not been

found above disseminated ores, although Tunell's columnar sections in three districts cut the exact place where these products would be expected to occur. But it is to be remembered that observation seldom falls within the brief lapse of time in which they could exist, and that, while there are many cases in which the inert iron compounds are found encroaching directly on the sulphide and evidently constituting the initial precipitates, nevertheless we know definitely that jarosite in some cases alters to another iron mineral. Finally, in numerous cases, the former existence of other less inert compounds is not disproved. We can gain a picture of the assumed temporary conditions, doubtless distorted, by studying mine oxidation and heap leaching.

Mine oxidation, in a face of disseminated ore, is favored by the following conditions: (1) the passage of unsaturated air; (2) tiny, drusy cracks, cutting the ore into angular blocks a few centimeters in diameter; (3) pyrite grains scattered along these cracks and disseminated through the blocks; (4) air filling the cracks and water filling the capillary pores; and (5) a temperature up toward 25°C. rather than down toward 10°C.

The temperature is a significant variant. While at 10°C. a reliable sample from copper ore might be taken after five years of exposure to air, at 30°C., such a sample may be obtainable for only a few days after the face is opened.

The effects of mine oxidation are evidenced in efflorescences on the surfaces of evaporation and in the oxidation of sulphide, not only on these surfaces, but also to a less degree in the inter-crack blocks.

Merwin and Posnjak (unpublished work) studied efflorescences collected by Blanchard and the writer in Bisbee (Arizona). These had gathered on a chloritic rock which was peppered with pyrite and so closely jointed that it broke in angular blocks a foot or two in diameter. Oxidation of sulphide had occurred in and along these joints and

had penetrated inward from the surface of evaporation only a centimeter or two.

The crust lay several centimeters thick on the wall of a drift. The temperature of its formation was about 30°C. Merwin and Posnjak determined in samples that it consisted of a complicated mixture of sulphates, predominantly ferrous next the rock, and increasingly ferric toward the airexposed surface. The principal minerals were: minor amounts of two ferric-ferrous sulphates, roemerite and voltaite; a small amount of basic ferric sulphate, copiapite; much normal ferric sulphate, coquimbite; and the cupric sulphate, chalcanthite.

Heap leaching, the other variety of artificial oxidation, is well exhibited in America by only one operation, that at Bisbee (Arizona). The procedure of leaching is as follows. Broken sulphide ore in a heap provided with "chimneys" for the circulation of air is periodically irrigated with water. Salts of iron and copper are drawn in the intervals of evaporation to the surfaces of the lumps and at the next irrigation removed in solution. (Hudson and Van Arsdale).

With these results of artificial oxidation in mind, we can resume the discussion of natural oxidation.

If the air, instead of being dry and causing evaporation, is wet and causes accumulation, the adhering films of solution may become so heavy as to drip away and join the ground water. With gushes of moist air, or of water from a rainstorm, or from a seasonal rise in water level, there are sudden changes of solution concentration. Sometimes, the interval in which the film is left undisturbed is too short for oxidation to get under way. Or, oxidation is always beginning and stopping, its more soluble products are repeatedly washed away and only its less soluble products, such as "limonite" or jarosite, can survive. Most of the oxidized copper compounds, being unstable, are removed.

The process outlined above is believed to characterize

oxidation above water level and to distinguish such oxidation from that below. As was stated above, its peculiarity is that of proceeding in multitudinous, tiny, discrete bodies of solution adhering as films or lying as fillings of capillary tubes and cracks, instead of in a flood of water. A result is a broad range of temperatures and wide variations in solution concentration.

The holding of the solution by molecular forces favors "cloister" oxidation and precipitation, that is to say, oxidation of a sulphide grain or small group of grains by the addition of air and water and without "interference" of substances derived from the gangue. (See plate XXII). Hence, oxidation of a mixture of chalcocite and pyrite may result in the precipitation of indigenous "limonite" occupying the place of the former sulphide. And, if the gangue does not participate, the sulphide itself is the sole variant, and differences of iron precipitate have more opportunity to accord with differences of sulphide here than in saturated rock.

Because jarosite is more soluble than "limonite," the fact that jarosite is present with "limonite" in the metores of disseminated sulphides accords with the conclusion that those metores were formed above water level.

The tendencies which promote high solution concentration above the water level are evidently carried further so as to promote the drying out of clay-like precipitates. The "limonite," which, especially in the oxidation of aggregated ores, may first appear as a jelly-like substance rich in water, breaks into tiny blocks whose surfaces of separation hasten the alteration: it, at length, becomes porous, rigid and crystallized, thus attaining the more permanent condition. Formed in a bath of water and remaining submerged, it would continue in the clay-like state for a longer time.

The attainment of temperatures higher than the average has been inferred by some observers from the presence of hematite in the metores, because hematite was produced in the Posnjak-Merwin experiments only at the higher temperatures. This inference, however, is unwarranted because hematite can be produced at room temperature if the chemical conditions are somewhat changed.

Actual measurements of higher temperatures in natural oxidation have seldom been made. Loughlin, however, made one in the Tintic District (Utah) where a shaft, first penetrating limestone, then shale with interlayered limestone, then quartzite, revealed above water level in the quartzite beneath the shale, "bad air" rich in carbon dioxide and nitrogen and at a temperature of 35°C. The heat and the bad air evidently result from the partial oxidation of scattered sulphides (pyrite, galena, sphalerite, and tetrahedrite) in the shale and intercalated limestone. A volcanic source of the heat is improbable because the latest volcanism was Miocene. The only reasonable explanation is that the gas is "used up air."

This subject, however, of heat effects and of differences of heat effects above and below water level is extremely speculative and is mentioned here because work is needed on it and because its development may yield direct guides to ore. For example, as has been often suggested, anomalous drill hole temperatures might indicate the position of oxidizing, aggregated sulphide bodies not cut by the drilling.

Then there are other effects of oxidation above water level not less problematical than those from heat. For example, in saturated rock, the withdrawal of S from the system as gaseous SO<sub>2</sub> is unlikely because, in the presence of water, it would be oxidized to SO<sub>3</sub> and so would be dissolved. But, in aerated rock, if the air is very dry, the escape of SO<sub>2</sub> is certain, in some degree, to occur. In this way the acidity of the solution could be reduced, and pyrite, which in decomposition below water level is likely to leave a void, might, in decomposition above water level, be, for this as

well as for the other reasons, represented by a "limonite" pseudomorph.

Such, so far as we know them, are the conditions and differences in effect of oxidation above and below water level. Inadequate as the information is, it helps us to discriminate between variations due, on the one hand, to the aeration or flooding of the oxidizing sulphide and, on the other hand, to differences among the sulphides themselves.

## CHAPTER VI

#### GANGUE

The subjects, chemistry and water level, have been examined for their contribution to the problem of reconstruction, and we may proceed to discuss the complications introduced by gangue. At the same time, we may consider the gangue from the standpoint of its use through habitual association as an indicator of kinds of sulphide.

#### COMPLICATIONS INTRODUCED BY GANGUE

The alternatives of result introduced by various gangues would seem complicated beyond hope, for, as was indicated on page 36, not only are the precipitates highly variable, but some of them have not been experimentally investigated. What amounts of  $K_2O$  and CaO must be added to the system  $Fe_2O_3-SO_3-H_2O$  to produce new solids, is not known and even the nature of such solids as might form is, for the most part, unknown.

Fortunately, field experience makes it possible to reduce these alternatives of result; and the simplification thus effected is sufficient to permit us to improve our skill in reconstructing the sulphide from the metore.

This simplification results from the possibility of dividing gangues into the classes: (1) inert (quartz and barite); (2) slowly reacting (fine-grained mixtures of quartz, sericite and adularia); (3) moderately reacting (coarser grained feldspar, after it has become more porous by partial kaolinization); and (4) rapidly reacting (carbonates).

By "reacting" is, of course, meant reacting in the acid solutions derived from sulphide oxidation. The outstand-

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ing function of the gangue is to furnish bases to combine with SO<sub>3</sub>; or, in other words, to use up acid: and to use up acid both at the time and at the place of the oxidation.

The ability of the gangue to use up acid both at this time and at this place is affected by the relative reaction rates of gangue and sulphide. These rates vary, not only with inherent chemical qualities, but also with accessibility, size of grain, and other conditions. But, in the usual disseminated ore, which has no carbonate, and which is so porous as to allow an abundant supply of oxygen, the results suggest, as is believed by Tunell, that the oxidation of the sulphide is usually completed before reaction of the gangue seriously begins, and that, when the iron leaves the place of the sulphide, it does so because there is not sufficient copper present to hold it in place. Thus, usually in sericite, and often in feldspar, pyrite leaves a void with the iron precipitated in a halo around it. Only in carbonate gangue (which is rare in disseminated ore) or where oxidation is especially slow (as when the sulphide is imbedded in wet clay so that oxygen must creep in by diffusion along capillary openings, instead of coming freely as gas) is the pyrite commonly perpetuated in a "limonite" pseudomorph.

Tunell is now investigating these questions on materials from Bingham (Utah), Morenci (Arizona) and Tyrone (New Mexico). He finds reason to conclude that when pyrite exists in great excess over chalcocite, the acid, produced after the oxidation of all the copper, slowly attacks the gangue and a large part of the iron is precipitated where gangue is going into solution and a smaller part where pyrite is going into solution. He finds further that the crusts of iron oxide lining the sulphide voids are, for any given ore, of about the same thickness in the various kinds of gangue minerals, while the transported iron oxide, which is thought to be precipitated mainly by gangue-neutralization, varies strikingly in amount in the various gangues, being abundant

in kaolin and sparse in sericite and quartz. This he takes as meaning that the indigenous iron oxide in these ores is largely controlled by the proportion of copper, iron and sulphur in the sulphides, rather than by the gangue.

We may, then, according both to field and laboratory evidence, conclude that the disseminated ore gangues often fail so to complicate the reactions as to destroy differences of effect made by differences among the sulphides themselves. In numerous instances, especially where the copper ratio was high, we have found the reactions within the place occupied by the sulphide to proceed almost unaffected by the gangue.

But, outside the place occupied by the sulphide, the gangue makes more difference. The iron liberated by oxidation, failing to come down as an indigenous pseudomorph, may make in the adjacent rock mineral a halo, tightly surrounding the sulphide cavity if the gangue is especially reactive, but spreading farther if it is more nearly inert. Or, instead of depositing in a halo, it may proceed into cracks.

# SUPERGENE KAOLIN AND QUARTZ

These two minerals result from the attack of acid solutions on the rock silicates.

Supergene quartz has been identified in the chalcedonic condition or as crusts of fine crystals inside the iron oxide linings of cavities left by sulphides in the disseminated cappings. In the hypogene mosaics of quartz, sericite and adularia which replace the major part of the rock, the picking out of quartz having supergene origin has not proved feasible and its presence there has not been determined.

Kaolin, on the other hand, in whatever part of the specimen it occurs, is presumptively supergene and produced during the decomposition of pyrite; for only insignificant quantities of it have been found to be produced in the cappings of the Southwest by ordinary weathering in the ab-

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sence of sulphide, or by hypogene processes. But it must not be thought that kaolin is an abundant constituent in the disseminated metores; its quantity has been commonly exaggerated because, among other reasons, kaolin and sericite are often difficult to differentiate in the hand specimen. When the kaolin constitutes as high as 25 per cent of the specimen, it indicates the former presence of especially abundant pyrite and shows that the ore was toward the aggregated, rather than toward the disseminated end of the series.

The kaolin replaces feldspar easily and sericite with much greater difficulty. With equal amounts of kaolin in two different metores, but with that kaolin replacing feldspar in the one case and sericite in the other, it is obvious that the second metore was originally the richer in pyrite. Indeed, in the metores derived from a mixture of chalcocite with pyrite, there is only a thin coating of kaolin on the sericite plates. But, when the pyrite is overwhelmingly abundant, as it may be in aggregated ore, the rock, including the sericite, may be replaced, with total destruction of texture, by jaspery "limonite," a fine-grained mixture of kaolin, quartz and "limonite."

In addition to the kaolin derived from the mineral which it replaces, there is also found a moderate amount of it in cracks and replacing calcite or other carbonates. The replacement in Leadville of mangano-siderite by kaolin derived from an oxidizing porphyry still peppered with pyrite several hundred feet above, as described orally by Loughlin, proves that transportation of alumina does take place in solution. Furthermore, even transportation of kaolin in suspension and by "pressure intrusion" is strongly suggested by certain of the occurrences in cracks.

It is well known that kaolinization occurs not only during the oxidation of the sulphide but also during chalcocite replacement and for our purposes it would be important to distinguish the products of the two processes. Unfortunately, no criteria for doing so in the metore have yet been established.

Indeed, the full possible importance of supergene kaolin and quartz as indicators of kinds of sulphide has only begun to be determined. The whole subject is made extremely difficult by the fineness of the mineral texture, and by the abundance of unidentified colloidal substance. The material ordinarily termed "kaolin" by the geologist is a vaguely defined mixture of kaolinite, halloysite (or colloidal kaolin), colloidal silica, "limonite," alunite, gibbsite, etc. Moreover, a complication is introduced by the occurrence here and there of hypogene kaolinite and alunite and of undetermined quantities of "iron kaolin" or nontronite.

Nontronite is an example of the necessity for careful study of "kaolin," for, as Larsen and Knopf have stated in conversation with the writer, this mineral is a common product of the oxidation of iron-bearing sulphide, and, though often described in German and French literature, it has been neglected in America. This opinion is supported by the available field evidence; and more and more nontronite is being found where its previous existence was not suspected. For instance, Lindgren's "chloropal" and "morencite" occurring in Morenci (Arizona) are identified with nontronite; and a pasty substance previously termed "limonite" occurring abundantly in a Jerome (Arizona) gossan was determined by Tunell as nontronite also.

The careful study, not only of this mineral but also of all the others with which it occurs, is very much needed, for, in terms of our problem, there is no means of predicting how far that study might lead.

#### HYPOGENE GANGUE

The characteristic gangue of the disseminated copper ores is the familiar fine grained mosaic of quartz, sericite, and

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adularia carrying abundant microvugs and following tiny, irregular cracks, or flooding the rock. The microvugs and cracks, together with the contacts between the small mineral grains, cause the material to be strikingly more porous than the rock before hypogene mineralization.

The fine-grained mosaic obliterates texture in the replaced rock. And when the mosaic is most pervasively developed. the copper minerals are often likewise most profusely disseminated and the completeness of texture destruction may, therefore, serve as a rough macroscopic guide to those parts of the outcrop which mean the best copper mineralization. For example, in Bingham (Utah), the spots showing the most complete texture destruction are commonly of highest grade, having not only the best dissemination of original copper minerals (chiefly chalcopyrite) but also the best chalcocite enrichment. Likewise in Miami (Arizona), the best schist ore has little schistosity left while the lower grade material is still strongly schistose. An outcrop map made in either place on the basis of texture destruction would have indicated the location of the better grade orebodies.

There are cases in which the alteration, though no less thorough than in the examples cited above, takes place with the texture surviving and with the rock retaining a fresh macroscopic aspect. One of these cases is Engels (California), where the alteration products, instead of being finegrained, are coarse and of the same size and color as the original minerals of the rock. Even this alteration, however, if carefully observed, may be used to delimit the orebearing ground.

There are other hypogene gangues which, though having no general meaning in terms of sulphide, may locally become very significant. For instance, Kingsbury in the Urals used fragments of barite found in small swamps to indicate gold veins directly below.

## CHAPTER VII

### Voids

Porosity, consisting in continuous, interconnected channels, is a prerequisite for disseminated copper mineralization. For, while pyrite can make its way throughout the rock, copper minerals remain in or close to channels and may be characterized broadly as "channel" or "open space" depositions.

Furthermore, this principle is exhibited not only on a small scale, as in the disseminated ores, but also on a large scale, as in the Butte veins. From the cracks, little or big, the mineralization spreads for some distance sideways into the rock, making porous, copper-bearing borders but leaving the intercrack blocks otherwise free from copper minerals.

The dependence of copper on porosity is not less significant in supergene mineralization than in hypogene. For, in the supergene process, disseminated ores follow the paths earlier established and it is only where continuous, closely-spaced openings exist that wide-spread deep enrichment results. That such openings are contained in disseminated ore, is shown by the following experiment: a hand specimen, dried at room temperature, is dipped in water and withdrawn; most parts of its surface become dry at once through the drawing of the water along capillary channels, and for several minutes there is a crackling sound made by the escape of air as the water continues to work its way inward.

How porosity can be made to serve in the search for copper ore is illustrated in the Bagdad District (Arizona). Here occurs a great area of disseminated pyritic mineralization varying from place to place in content of chalcopyrite and VOIDS 71

chalcocite. In the leached outcrops, "limonite"-bearing quartz veinlets have been found to indicate in some cases pyrite and in some cases copper-bearing sulphide below. But, if that part of the district, which for other reasons such as outcrop copper is known to be most promising, be taken

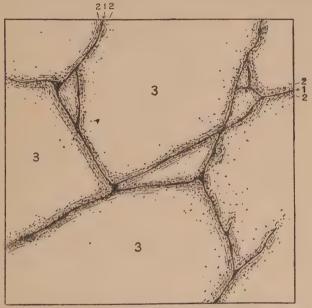


Fig. 8. Sketch showing a structure common in "disseminated" copper ores and the dependence of copper on cracks. Rock originally a porphyritic monzonite. Actual size. 1, vuggy cracks carrying quartz; pyrite, chalcopyrite, and chalcocite; 2, borders of rock made over into a fine-grained mixture of sericite, adularia, quartz, and pyrite, with microvugs containing quartz, pyrite, chalcopyrite, and chalcocite; 3, chloritized rock with fine-grained disseminated pyrite and with rock texture well preserved.

by itself, then its richer portions are found to abound conspicuously in networks of "limonite"-bearing quartz veinlets and, though the copper is largely weathered out, the system of channels which was essential to both hypogene and

supergene copper mineralization remains unimpaired to indicate clearly that ground which, previous to oxidation, was higher grade.

In this kind of mapping, it must be remembered: (1) that features will differ from district to district; and (2) that the fresher the rock the more prominent the feeding channels and the more strict the confinement of copper to their immediate vicinity. In those metores of Bingham (Utah) and Miami (Arizona) which have complete texture destruction, the rock becomes more porous throughout and the original channels less conspicuous within it.

But, though supergene enrichment follows the paths earlier established, there are new paths established by weathering, and the distinction of the latter from the former is necessary; for a porosity existing in the metore alone would not have necessary meaning in regard to the localization of the sulphide. And even this distinction by itself is insufficient. We must refine it by learning the differences between voids from the removal of sulphide and those from the removal of non-sulphide; and between voids from the removal of one sulphide and those from the removal of another; and we must examine the effects of oxidation slumping and collapse.

#### PRE-OXIDATION VOIDS

"Pristine" openings, such as vesicles and inter-pebble spaces, do not exist in the rocks of disseminated copper deposits. The prospector is often misled, however, by outcrops of copper-stained lava whose vesicles he believes to be sulphide cavities. There is no problem here, for careful observation makes clear their origin.

A less obvious kind of cavity, which should be remembered although it has not been found in disseminated deposits, is that described by Lindgren and Loughlin in Tintic (Utah). There, pre-volcanic, pre-ore weathering

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produced caves and residual, kaolinic gouges which could be readily confused with effects of post-ore oxidation.

Hypogene mineralization cavities are more difficult to see and study than supergene. In disseminated deposits, the openings consist in the microvugs, cracks, and mineral contacts mentioned earlier in this chapter and the largest found are a few millimeters in diameter. Such vugs, lined with quartz crystals projecting inward, were found by Tunell in Morenci (Arizona), Bingham (Utah), and Tyrone (New Mexico) never to have contained sulphide. But, in other districts, not yet carefully studied in this respect, there may be doubt whether the vugs were originally empty or were emptied of sulphide during oxidation. This problem has to be approached through a study of other factors, such as the known habit of association between these linings and sulphides in the ground under examination and such as the "limonite" vestiges in neighboring cavities or the "limonite" halos around them.

In certain districts the problem of recognizing hypogene origin is simplified by the extreme smallness of the hypogene openings. For instance, in the explored portions of Bisbee (Arizona), the hypogene products in both limestone and igneous rock are characteristically dense, the largest hypogene vug being scarcely sufficient for the insertion of a knife point, while the supergene products are cellular, loose, filled with caves small and large, and possessing, therefore, a sharply contrasted kind of porosity. All but a very few of the openings whose walls were found separated by a macroscopic interval have proved to be supergene.

Several disseminated prospects have shown cavities of angular outline made by the hypogene solution and removal of feldspar phenocrysts, and these cavities, carrying a little copper and "limonite" in the outcrop, have been taken by the prospector to correspond to sulphide. They are common in bodies carrying tourmaline and pyrite and their identifica-

tion requires only careful observation. The following places among others have proved to possess such readily recognized porosity: Majuba Hill (Nevada), Hussey Mine (Sierra Co., Nevada), and the Transvaal District (Sonora). In these cases, deeper exploration showed grains and needles of enargite, pyrite or other sulphides partially filling a few of the cavities. In one of the cases, the Hussey Mine, where tourmaline was absent, hypogene alunite and sulphur were present and pyrite was abundant.

Hypogene openings of much larger size are known also but these occur under conditions which make their origin unmistakable. They are particularly marked in the mineral pipes, such as the Pilares Mine (Sonora), the South Ibex Mine (Leadville, Colorado), and the Cresson Mine (Cripple Creek, Colorado). These contain quantities of breccia whose fragments are jumbled and the spaces between are lined and filled with quartz, pyrite and other sulphides. In the breccia lie numerous quartz-lined vugs, which show a tendency to be larger where the depth of mineralization was less. For instance, at the South Ibex, the mineralization occurred 10,000 feet deep and the largest vug is two feet across, while at the Cresson the mineralization occurred 1000 to 2000 feet deep and vugs have been found 100 feet across. It is the breccia or rubble structure with its cementing crusts of quartz crystals pointed toward the centers of vugs that makes this material unmistakable.

# OXIDATION VOIDS MADE BY THE REMOVAL OF NON-SULPHIDES

In aggregated ores, calcite, siderite, gypsum, and anhydrite tend to disappear during oxidation and leave a void or cause collapse. In extreme cases even feldspar may be dissolved out. But, in disseminated ores, gypsum and anhydrite are absent and calcite and siderite are rare. Moreover, even when calcite or siderite do occur, they are usually

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replaced, during oxidation, by "limonite" pseudomorphs and they leave no opening. Therefore, macroscopic voids made by the removal of non-sulphides are little developed in the disseminated metores.

Pores of sub-microscopic size are well known to be made during kaolinization. Kaolinized feldspar is more reactive than fresh feldspar, because of such pores and because of new cracks made by slight volume adjustments. Similar pores are common in "limonite." Posnjak and Merwin found index fluids to soak through the ferric oxide precipitates in such a way as to change the apparent index of refraction. Unfortunately, the problems of such openings have not yet been investigated from our standpoint.

# OXIDATION VOIDS MADE BY THE REMOVAL OF SULPHIDES AND CHARACTERISTIC OF PARTICULAR SULPHIDES

The only common, euhedral sulphides are pyrite, pyrrhotite, sphalerite, enargite and covellite. Of these, the only sulphides which often disappear without leaving a "limonite" pseudomorph are pyrite, pyrrhotite and ironfree sphalerite. But pyrrhotite and sphalerite are uncommon in disseminated ores and, inasmuch as the only cavity-making euhedral sulphide abundant in these ores is pyrite, the use of the cavity to identify the sulphide is limited to euhedral occurrences of that mineral.

In detail and by themselves, the cavities left by sulphides are actually of little help and their significance has been much over-rated by prospectors. But they have a general significance in one respect: if the proportion of pyrite to other sulphides is sufficiently high, all the sulphides, including chalcocite, will be represented by voids, and a high proportion of sulphide voids usually means a high proportion of pyrite.

The extreme result of the removal of sulphides is the siliceous sponge found spottily developed in gossans. The sponge is made by the removal of pyrite, and sometimes of sphalerite. It carries cells, cubic or irregular, measuring as much as half a centimeter across and having septa which represent the former divisions between sulphide grains; it varies from a mere pepper of cavities through gangue, in which the walls exceed the cells in diameter, to a true sponge, like pumice, so light that it floats on water and so friable that it easily crushes down into sand (plate VIII-A). Often blebs of the sponge are enclosed in bodies of quartz strong enough to protect them from crushing.

## OXIDATION COLLAPSE AND SLUMPING

If the cavities made by oxidation are sufficiently large, or if their walls are sufficiently weak, the walls collapse and the overlying ground slumps into the opening. But, though volume changes of such origin occur in the oxidation of the disseminated ore, they must be small there, for neither disarrangement of fragments nor development of extensive new cracks has been noted. There is, indeed, no reason to expect oxidation collapse and slumping to play any important partin the reconstruction of disseminated metores.

As a guide to aggregated ores, however, oxidation collapse and slumping require much attention; for oxidation in such ores not only commonly results in (1) a removal of substance in the metore with a reduction of volume and the achievement of a loose, shrunken condition, but also, (2) where the rock is limestone or other carbonate, in the removal of substance in the walls and the creation of caves there.

These results have been best studied in Bisbee (Arizona) where Ransome has outlined the process very clearly as follows: "The oxidized material is not only more porous but much softer and more plastic than the original mineralized limestone and hence greatly weakens by its presence the rocky structure in which it occurs. The overlying lime-

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stones, no longer adequately supported, fissure and settle down upon the soft plastic ore and gangue."

Every oxidized Bisbee orebody examined by us from this standpoint has been found to have collapsed or slumped

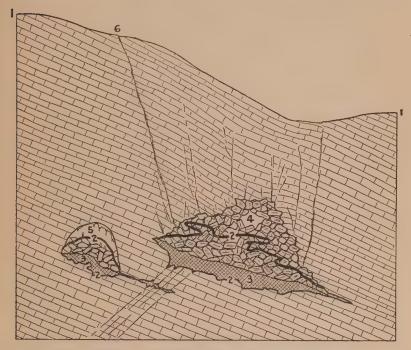


Fig. 9. Sketch cross section illustrating oxidation collapse and slumping. 1, surface; 2, original outline of aggregated, sulphide orebody; 3, present shrunken, oxidized orebody; 4, collapse breccia (boulder aggregate or angular fragmental breccia cemented by supergene calcite or quartz, 5, cave; 6, collapse and slump cracks (open or filled with gouge or quartz; where reaching the surface filled with mud or conglomerate "dikes").

ground above it. Such ground was first identified in crosscuts lying above ore and showing a jumble of rock fragments resembling "old fill" or caved ground above a mined-out stope. The fragments of broken rock are angular slivers, wedges and bulky pieces, and they vary in diameter from a centimeter to 10 feet: they are separated from each other by "water courses," by vugs, great and small, or, sometimes, merely by cracks. That this material is independent of mining operations is proved by the fact that it is so strongly cemented with thick crusts of calcite that it stands without timber. (See plate XIV.)

This jumbled or collapsed ground was found going upward from the oxidized ore body as much as 100 feet and terminating in an irregular dome-like roof of more solid ground; or, failing to reach quite up to the roof, it leaves an intervening subsidence-cavern.

Above the roof, steep marginal cracks ascend to the surface, outlining an irregularly cracked body of ground which has undergone slight subsidence. Where the marginal cracks traverse limestone they are cemented with calcite and they serve to indicate at the surface the position of oxidized ore below, even when it lies at a depth as great as 700 feet. In jasperoid, the cracks though not less developed are less usable, for they carry less calcite and are more difficult to identify. This subject was found so promising that a special study was undertaken in Bisbee (Arizona) by H. M. Kingsbury and E. H. Wisser, and this study is still in progress.

A detail of the picture as revealed by this study is shown in the following illustration. In several parts of the Bisbee district are large bodies of rounded limestone boulders, often corroded and deeply embayed and imbedded in a plastic matrix rich in alumina compounds, "limonite" and black manganese minerals. Here and there are spots of very rich oxidized copper ore. This is called the "mud and boulder country." Though its relation to sulphides has never been systematically studied, its origin as the caved-in wall of openings made by oxidation shrinkage is unquestionable.

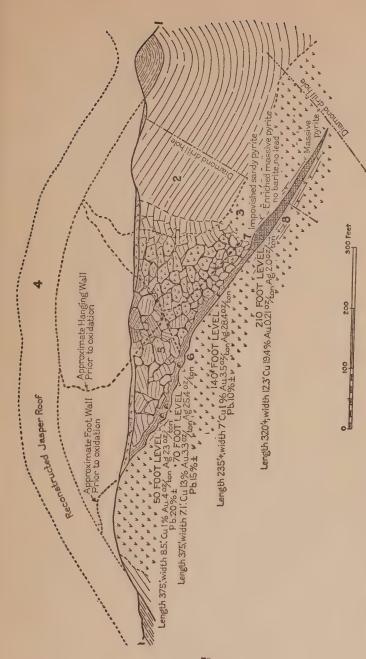


Fig. 10. Cross section showing oxidation collapse over South Orebody, Tuba Mine, Tanalyk-Baimak, South Urals, Russia. (Kingsbury.) 1, surface; 2, induraued tuffs; 3, daciue; 4, jasper; 5, oxidation collapse rubble; 6, barite sand, de, creasing with depth; 7, impoverished sandy pyrite; 8, massive pyrite.

Other examples of oxidation slumping are: the Bully Hill Mine (Shasta County, California), where the gossan of massive pyrite-sphalerite-chalcopyrite-quartz-gypsum ore is shrunken and depressed below the level of the adjacent ground, on account of the removal of sphalerite and gypsum; the Grong Mines (Norway), where Morse describes a "cart track" marking in marshy ground the position of a massive pyrite vein lying below and equalling it in width; the Tuba vein (Urals) illustrated in figure 10; and the Kyshtim veins (Urals).

The Kyshtim veins, as already discussed on page 52, consist of pyrite and chalcopyrite with minor quartz and barite. All the veins decrease sharply in width as they pass upward from the sulphide which may be as much as 20 feet wide, to rusty quartz-barite sand, which is no more than two or three feet wide. At the water level the veins, in some cases, expand to their original width and become firm gossan. In other cases, where the water level lies at or close to the surface, the gossan is missing and the vein apex may lie hidden in a swampy depression.

The literature has strangely neglected this subject of oxidation collapse as a guide to ore and American prospectors are unprepared by experience to discover ore-bodies whose "heads are hidden" by such collapse or whose presence is signalized merely by cracks reaching the surface. The subject of collapse is one of the most promising, for the discovery of new aggregated ore, in places where there is other reason to suspect such ore, as where an outcrop rich in iron quits along the strike at low, gravel-covered ground. Or, to put it in another way, we have here the very practical problem of reading the surface when subsidence or collapse make it weather to a depression.

## CHAPTER VIII

# METALS IN NON-SULPHIDE FORM

Before we pass to relict sulphide and "limonite," which, as was already stated, are the main sources of direct evidence for reconstruction, we have one more subject of which to dispose. This subject is concerned not only with the oxidized copper but also with such gold, silver, arsenic, lead and zinc as persist through to the surface in spite of oxidation.

Its importance rests on the fact that these metals, while often paired in the sulphide ore, are commonly separated during oxidation, copper, and zinc being leached out, silver and arsenic sometimes leached out and sometimes retained, and lead and gold remaining behind. As a result, the metal that endures may indicate that which has gone. For instance, if gold and copper occur together in explored sulphide, then gold in the outcrop of unexplored ground nearby would suggest that copper had departed.

In the development of this subject, the gangue must again engage our attention. For the behavior of a particular metal differs according to the gangue in which it lies. Thus, 0.1 per cent copper in a quartz metore may be the residuum of 2 per cent in the sulphide, while 0.5 per cent copper in a calcitic metore is likely to be, not a residuum, but the full amount.

#### GOLD

Gold in metore, because it is so hard to see, has been studied by assay, or visually in rich specimens. In disseminated metore not even assays have been made. As a guide to disseminated copper, therefore, gold can be considered merely as a subject with possibilities for develop-

ment. In aggregated metore, on the other hand, it is better known and its importance better appreciated. For its value in the judgment of gossans, therefore, and for light which the gossan information sheds on cappings, we find it desirable to consider this subject at some length.

Gold is now and then found in the metore in sheets, wires, and plates later than oxidation minerals such as "limonite," yielding satisfactory proof of oxidation transportation. It is, however, the most stable heavy metal, not excepting iron, and experience indicates that:

- 1. In the oxidation of sulphide, mechanical concentration of gold is more commonly recognized than chemical migration. For instance, though Butler and Loughlin studied the diverse deposits of Utah for several years, they found little proof of gold migration during oxidation.
- 2. Even with chemical migration proved, evidence of extensive movement is not necessarily available.
- 3. Mechanical concentration is proportional to the removed amount of substance other than gold and is marked toward the gossan end rather than toward the capping end of the metore series.
- 4. Chemical migration is possible only in an acid, non-reducing solution and is stopped when that solution is neutralized or becomes reducing. The actual proved migration, indeed, almost invariably occurs in aggregated ores because it is there that the solutions maintain their acidity for the longest periods. Here again the nature of the gangue is important. The presence of abundant feldspar makes the migration of gold improbable and the presence of abundant calcite makes it impossible.
- 5. The conditions favoring the solution of gold occur near the top of the sulphide for there the solutions are both acid and non-reducing. And since, immediately below, there exist sulphides and ferrous sulphate, two vigorous precipitants of gold, extensive downward migration is inconceiv-

able while lateral movement along the top of the sulphides with spotty impoverishment and enrichment may take place.

- 6. Variations of these results may be introduced by jarosite or residual sulphide in the metore well above the main body of sulphide; for these minerals on weathering may yield acid and this acid may persist over a larger vertical range. One of the possible variations is the chemical accumulation of gold from the metore in a thin zone lying at the top of the sulphide and descending as the sulphide surface is depressed by oxidation. Whether or not this variation is important has not been established.
- 7. Manganese dioxide is one of the few chemical agents which promote gold migration for, in the presence of chlorides, it liberates nascent chlorine, one of the few solvents of gold. The reasonableness of this as an explanation makes it easy to exaggerate the amount of migration and to assume migration in cases where the distribution of the gold is accidental, or is controlled by mechanical migration or by residual concentration. Field experience indicates, in fact, that the presence of manganese fails to simplify the judgment, for practically, where manganese is found in the metore, the question still remains as to whether the metore has been enriched, leached, or left unchanged in respect to gold. The only course left is to depend on the rule that chemical migration is to be accepted only where it is proved by the evidence of the specific case. This conclusion was reached by Hoover who termed the chemical migration of gold a "favorite field for speculation" involving the "reconstruction of conditions wholly unknown." The problem of using outcrop manganese as a practical guide to gold below has not been solved.

It has been proved that in the disseminated ores a little gold goes with the copper and that, excepting in the surface layer, there is not even mechanical concentration. Although no comprehensive sampling of disseminated ores has been made with the idea of determining just how closely the gold and the copper vary together, this is a simple subject and one of promise in the judgment of outcrops; for, in a given district, if fixed relationships between copper and gold were once established, the content of gold, as determined in samples of leached outcrop, could be used to indicate the former copper content of various areas.

#### SILVER

Silver is, of course, far less stable than gold and its migration during oxidation far more extensive. It acts more like copper than gold does and, though resembling both metals in requiring an acid solution for its transportation, it differs from both in having an erratic behavior. In some cases, it is transported. In others, apparently similar, it remains in place; and even when the conditions are favorable to leaching, as in the production of the Kyshtim sands from which the iron of the pyrite was mostly removed, silver may still survive.

The wide range in the behavior of silver is seen in the following examples:

In the Rochester district (Nevada), Knopf found a homogeneous deep sulphide enrichment of silver resembling that of copper. Here, steep veins of fine-grained quartz, well stained with "limonite," carry minute scattered grains of pyrite and extremely minute, even invisible, grains of silver chloride and argentite. The silver chloride is an alteration of argentite and the argentite a supergene replacement of sphalerite. The enriched ore occupies zones in the veins several hundred feet high.

Such deep enrichment as this is exceptional. A more common case is found in the United Verde Extension mine in Jerome (Arizona), where native silver is so strongly concentrated in specks and veinlets just above a massive chalcocite orebody that the gossan itself is stoped a set or two above the sulphides.

Of course, the commonest form of enriched silver is the chloride, which is less soluble than chlorides of copper. This makes spotty concentrations, as along gouges or cracks, and its occurrence is unpredictable according to any general rules. Sometimes a flat, tabular concentration occurs near the surface: there may be a "pancake" lying a few feet deep and moving downward ahead of erosion; or, the silver solution may be drawn up in capillary openings and precipitated in the upper few feet of the ground. There are, doubtless, other possibilities, and a given effect may result not from one process but from two or more in combination.

In many cases, under a variety of conditions, there is but short migration, as was found by Butler and Loughlin to be rather the rule throughout Utah. Much could be done in the explanation of this difference in behavior if more were known of the form in which the silver occurs. A step in this direction was recently taken through the discovery by Schaller and Loughlin of a new silver mineral, argento-jarosite, which will now no doubt be recognized in many places. But so long as the form remains so often unknown, rules for silver can hardly be hoped for.

Silver, like gold, is present in disseminated ores but, unlike gold, because of its erratic behavior, it will remain unpromising as an indicator of copper until more is known of the chemistry of its oxidation and enrichment.

#### ARSENIC

Arsenic, though sometimes leached out, often survives in abundance to the outcrop. For example, in Gold Hill (Utah), large bodies of scorodite are present.

The ferric and copper arsenates are rather insoluble and their survival is not contrary to expectation. Qualitative tests for arsenic are always warranted. Arsenic may prove useful, where the only arsenic-bearing sulphide is enargite, in serving for the distinction between copper-bearing ground and that which is merely pyritic.

#### LEAD AND ZINC

The behavior during oxidation of the principal lead and zinc bearing sulphides, galena and sphalerite, is simple. Briefly, galena, though largely replaced by indigeneous lead carbonate or sulphate, survives as residual cores, even in the outcrops. Under the conditions prevailing in the West, a vein is usually lower in lead at the actual out-

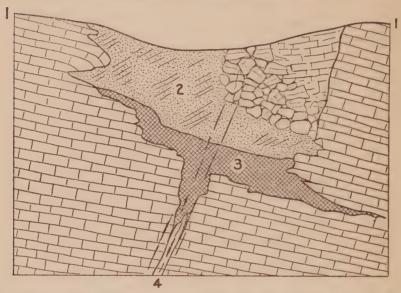


Fig. 11. Sketch showing relations of lead and zinc after oxidation of a galena-sphalerite orebody in limestone walls. 1, surface; 2, oxidized lead ore in place of former galena-sphalerite ore; 3, oxidized zinc ore replacing limestone; 4, fissure.

crop than a little deeper. Yet the impoverishment is not sufficient to prevent discovery from lead minerals in the outcrop and mining from the "grass roots." The sphalerite, on the other hand, is destroyed, leaving voids or indigenous "limonite," and the zinc is almost completely removed.

If limestone occurs below or alongside, the zinc may be caught in it and may precipitate as carbonate or silicate.

Disseminated copper ores seldom carry significant quantities of galena or sphalerite. Where sphalerite does occur, however, it is readily replaced by covellite, chalcocite or argentite. For example, in a district where galena and sphalerite are known to accompany chalcopyrite and pyrite in the primary ore, outcropping lead carbonate might be taken as pointing to primary galena, sphalerite and chalcopyrite below, and as suggesting the replacement of sphalerite by covellite between the metore and the primary ore.

#### COPPER

The disseminated ore usually produces enough acid during oxidation to carry away most of the copper. But, out of numerous metores examined by us, few have been found in which at least traces of the copper failed to remain behind either in a brown, undetermined and inconspicuous form, or in visible silicate, carbonate or sulphates, and this rule applies not only where the "limonite" replaces the sulphide, and therefore denotes low acidity during oxidation, but also where the "limonite" is transported, that is, where the acidity was high. This means, not that every hand specimen carries copper, but that out of several specimens, one will be found that shows it. In other words, copper once in the ore almost never wholly escapes and, if none occurs in the capping, experience suggests that none existed in the sulphide from which it was derived.

Now, the questions in which we are most interested are: given a small quantity of copper in the capping, (1) is that the total amount of copper present before oxidation? (2) is it more than that amount? or (3) is it a mere relic of that amount?

These questions are in some degree answered by the capping itself. If oxidized copper occurs there in a disseminated pattern resembling that of the sulphide, little could have escaped, for wide-spread, uniform, partial leaching of copper has nowhere been found.

If the metore carries abundant calcite or other carbonate, leaching does not occur. It is by this principle that Butler is guided in his interpretation of two Utah districts. In one of these districts, he takes the presence of calcite and of other carbonates in the primary ore to be the reason why sulphide enrichment has not taken place and why abundant copper carbonates have formed. In the other district, he deduces from the abundance of carbonates in the surface zone that only minor sulphide enrichment will be found below.

If the calcite, instead of being scattered, is concentrated in spots, it may make knots of rich oxidized copper mineral. Or, calcite in the walls may make ore similar in origin to the carbonate zinc ores mentioned on page 86.

Feldspar in the metore, if it is stained with copper, suggests, but does not prove, that leaching has not occurred. Unstained feldspar means little, for much copper in acid solution could pass out along cracks before all the feldspar became kaolinized. While calcite prevents leaching and enrichment, feldspar seldom does so.

A feldspathic or kaolinic gangue is sometimes found, however, which has acted as a precipitating agent for a concentration of oxidized copper. An outstanding example of this process is the Black Warrior copper pitch ore (Miami, Arizona), in which copper replaces kaolinized dacite and dacitic conglomerate along steep fractures immediately above schist. The copper was liberated by oxidation from disseminated ore bodies in schist nearby and is termed "exotic" by Ransome. An even more striking case is found in Bisbee (Arizona), where a raise filled with altered limestone (largely rock silicates and calcite) in six years was found to have changed to a kaolinic, "soapy" body, replaced in spots and along tiny branching veinlets by oxidized copper minerals. The fill, making a 5 to 6 per cent ore, was mined and sent to the smelter.

While we are on this subject of exotic copper ores, we should note their peculiarities. They can be recognized by an extremely low content in gold and silver, and by the fact that their copper is distributed in rich knots or in paint, rather than in the pattern of disseminated ore.

Experiments were made by Morse to measure the precipitating power of various metores. He boiled powdered capping for five minutes in a 5 per cent solution of CuSO<sub>4</sub> and found that, though the capping had lost much copper by natural oxidation it could in this experiment precipitate several per cent of its weight in copper, so long as the precipitating agent was feldspar. But, when the precipitating agent was calcite, any such precipitating power was found to mean that no leaching had ever occurred.

A gangue of sericite or quartz has still less ability than feldspar to prevent leaching of copper, and it is an important fact therefore that leached capping gangues are rich in these minerals. There is, indeed, so little precipitant in some of the ores that even the iron, which is well known to be far more easily precipitated than the copper, is sometimes leached out, leaving behind a kaolinized mass or a quartz sponge. This result, however, is common in aggregated rather than disseminated ores.

In the reconstruction of the capping the oxidized copper content is a useful and definite guide. Particularly is this the case in prospects showing 0.25 to 1 per cent copper along with a strong excess of rapid precipitant such as calcite; for, in that case, an improvement in the quantity of copper is not to be expected with depth.

This subject of the retention of copper by gangue is another field for investigation and one which promises to yield important results.

## CHAPTER IX

## RELICT SULPHIDE

Of all the evidences for the reconstruction of sulphide from metore, that of actual gradation between metore and sulphide is more direct than any other; for it makes the shortest chain of reasoning and leaves the least opportunity for error along the way. The specimen containing both sulphide and metore gathers the roving speculations from far and wide and ties them down to habits of association between certain kinds of sulphide and certain conditions of gangue, porosity, precious metal content, base metal content and "limonite." The actual adjacency and gradation simplifies and economizes the process of judgment. A hundred surmises fall away and various qualities, even including color of "limonite," which could never be made to serve in general, become, in the particular orebody, narrowly diagnostic. In such degree as is possible, therefore, the reconstruction must rest on sulphide found in the actual ground in which ore is being sought.

Now, where the ground is little explored, sulphide will be hard to find, for the small amount left in the capping is mostly cleaned out in the surface layer. Yet, with its importance understood, and with rocks persistently broken for this especial purpose, it is astonishing how many specimens of sulphide can be revealed. If a leached outcrop is worth examination at all, it is worth, first of all, the painstaking search for relict sulphide, and, though this require days of labor and the digging of many holes, it will excel in result an equal expenditure of energy in another direction. It creates a wholesome supply of facts and relict sulphide thus becomes material of the first importance.

Given, then, specimens of relict sulphide, how can we use them in reconstruction? They will be small in quantity, constituting perhaps not more than one grain out of each original thousand. How true, then, a sample does this grain constitute and what does it signify in terms of sulphide destroyed? If grains of pyrite and chalcocite exist in the proportion of 10 to 1, the question is—in what way does this proportion differ from that existing previous to oxidation?

This question is best studied in the particular district for, in this matter, too, the district habits differ from place to place. But there are certain general factors, both chemical and mechanical, which have to be examined as a stimulus to field observation. We shall first consider these factors and then correlate them with the field evidence which is available.

The change, metore to sulphide, though taking place in a zone which may attain a thickness of many feet, is found in detail to occur by the gradual lessening in volume of sulphide-bearing residuals of rock free from oxidized minerals and surrounded by rock in which the sulphide has been completely destroyed. The actual boundary between the sulphide-bearing rock and the oxide-bearing rock shows a complete transition within a distance varying from a centimeter to less than a millimeter.

This means that oxygen has come in such overwhelming excess that in general the most enduring sulphide grain survives only a centimeter or a millimeter, or even less, beyond the least enduring. Yet often a small remnant sifts through the mixed zone and survives above it. It is this remnant, chemically or mechanically protected, which we get at the surface as the relict sulphide.

We shall first consider the means of chemical protection. Of these, the best known are: (1) low oxidation rate; (2) high electric potential; (3) high persistence in the presence

of sulphuric acid; and (4) high persistence in copper sulphate solutions.

The most valuable experiments on oxidation rate are by Allen, who carried further the work of Buehler and Gottschalk (1910-1912). In these experiments (1914), Allen attempted to measure the rate of oxidation of the common sulphides with several oxidizing agents. He described the methods used and the results obtained in a private communication as follows:-Blocks of natural sulphides of exceptional uniformity and purity were selected, cut, ground and polished so that the surface could be accurately measured. In the experiments account was taken of temperature. concentration, crystal direction and other important conditions. The attempt was a failure, partly because it was not found possible to prevent entirely the precipitation of sulphur on the sulphide surfaces but chiefly, as it was judged. on account of the impossibility of reproducing comparable surfaces, even on the same block. Microscopic examination by Merwin indicated that the difficulty in getting comparable results was not caused by an actual difference in area due to pits and flaws of unequal size or number on surfaces supposed to be exactly alike. There is a difference in chemical behavior between a rubbed surface and the layers beneath it and in whatever the difference consists it is apparently impossible to duplicate such a surface exactly. By crushing and very careful sizing between two bolting silks of meshes not far apart (100 and 125 meshes per inch), counting the number of grains in a given weight and assuming a minimum spherical surface for each grain, a rough measure of surface may be attained and in this way a comparison was made of the rates at which the different sulphides oxidize. Different preparations of the same sulphide thus compared give results which show reasonable agreement, and the different sulphides when arranged according to the rate of oxidation take, with slight qualification, the same order, whichever of the oxidizing agents is employed. Marcasite is slightly erratic, probably on account of its greater tendency to precipitate free sulphur; it may either precede or follow pyrite, while covellite, sphalerite and chalcopyrite, which possess rates of a similar order of magnitude, low compared to the rest, do not follow the same order with all three reagents. Chalcocite, which with slightly acid reagents starts near the top of the series, in neutral solutions oxidizes very slowly indeed.

Figures obtained in this way can, as Allen says, have no standing as constants and consequently have never been published, but the order of oxidation has a certain interest to the geologist, and if due heed be given to the influence of differences in composition and to galvanic effects between different sulphides, the order may be found to hold in nature.

Table 4 indicates the determined order of rates.

The best work on the electric activity of the sulphides is by Wells, who likewise carried further the work of Buehler and Gottschalk. The electric activity of the sulphides, as Wells makes clear, is a complicated subject, the potential varying in the same sulphides with the nature of the solution and with the degree of "polarization." There is no fixed series of sulphides in which the given sulphide is known through electric activity to gain protection from certain sulphides and to give protection to others; for the order of arrangement differs with different conditions. Wells' results were obtained without access of oxygen and the admission of oxygen might, of course, make changes. Furthermore, there is no assurance that electric activity will dominate: for example, though the difference of electric potential between oxygen and hydrogen is great, their rate of reaction at low temperatures is so small that they long remain in contact without beginning to combine. Indeed, for application to the outcrop problems, electric activity cannot be correlated in detail with field conditions.

Nevertheless, from this subject emerges an outstanding fact, namely, the behavior of pyrite as an "unattackable electrode" which is protected and remains bright while other sulphides are being altered. This is harmonious with the

TABLE 4

Showing results of Allen's experiments on the oxidation of sulphides (from private communication)

	FERRIC SULPHATE	AMMONIUM PERSULPHATE		HYDROGEN PEROXIDE
		Neutral	0.1 per cent H <sub>2</sub> SO <sub>4</sub>	0.1 per cent H <sub>2</sub> SO <sub>4</sub>
Very large change	cc bn	bn ·	cc bn	ec bn
Medium change	py mar	mar	ру	mar py
Small change	cv sl cp	cv sl cp cc	cv sl cp	sl cp cv

cc, chalcocite; cv, covellite; bn, bornite; cp, chalcopyrite; sl, sphalerite; py, pyrite; mar, marcasite.

Supplementary notes: Marcasite and pyrite are so close in rate that a difference is difficult to detect, but marcasite becomes coated with sulphur and is thus protected. Galena at first goes rapidly but later very slowly because it becomes covered with oxidized lead products. Sphalerite goes very slowly if pure but more rapidly if it is iron-bearing. In the oxidation, chalcocite turns blue on the surface (changes to covellite) and bornite turns yellow (changes to chalcopyrite). Mixtures of the sulphides oxidize faster than the single sulphide. Chalcocite oxidizes faster than the rest in the presence of free acid, but otherwise slower.

selective preservation of pyrite in relict sulphide, which is commonly found in the field.

The reactivity of sulphides in the presence of sulphuric acid was examined by Zies, Allen and Merwin in their experiments on secondary copper enrichment, with close sizing to get equality of exposed area. Their results are given in table 5.

As is well known, chalcocite and covellite are relatively inert in sulphuric acid, and pyrrhotite, sphalerite and galena are rapidly decomposed by it. Allen found pure sphalerite to be less soluble than that containing iron and to be less soluble than is commonly supposed.

So long as a mineral is being decomposed by sulphuric acid, other minerals more inert in the same environment are kept in a reduced condition by the H<sub>2</sub>S generated and are, therefore, protected. This process may dominate in the case of sphalerite, for sphalerite is usually found in metores

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		TABLE 9								
	SOLUTION H <sub>2</sub> SO <sub>4</sub>	TEMPERA- TURE	DURATION	RESULTS						
Pyrite	per cent	200°	3 days	Very slight at- tack						
Chalcopyrite	2	100° 200°	2 weeks	No determinable attack Much more attack						
Bornite	2.5 2 2 1	200° 200° 100° 40°	2 days 8 days 2 days 2 months	than at 100°  Marked attack						

to be destroyed in advance of other sulphides. It is less important in the case of galena, though that mineral is equally soluble, because galena becomes protected by lead sulphate.

The reactivity of the sulphides in copper sulphate solutions was studied by Zies, Allen and Merwin in the experiments already quoted, and has to do with the replacement of the sulphides rather than with their solution. These investigators concluded that, because of various difficulties including that of getting equality of exposed area, they could

not get accurate data on the relative reactivities of the sulphides. However, they found indications of relative values based on the quantity of copper precipitated, as is shown in table 6.

Of the enrichment products, Zies, Allen and Merwin found that the order of persistence in cupric sulphate solutions is (1) chalcocite (by far the most persistent), (2) covellite, and (3) chalcopyrite. They found, also, that the effect of cuprous sulphate was to accelerate the alteration of all the sulphides and that the effect of sulphuric acid was to

TABLE 6

List showing results of Zies-Allen-Merwin experiments on relative reactivities of the sulphides with cupric sulphate at 40°

SULPHIDES	REACTION									
Galena	Far more reactive than any other sulphide considered									
Pyrrhotite	Differs markedly									
Charcopyrite	Intermediate									
Bornite	Follows chalcopyrite in precipitating power but follows galena in volume of mineral altered									
Pyrite and covellite	Action very slight									

accelerate the alteration of sphalerite, pyrrhotite and bornite but to retard that of chalcopyrite and pyrite.

In the discussion of relict sulphides we have, so far, been dealing with chemical protection. We shall now proceed with mechanical protection.

It must be realized that the relations between chemical and mechanical protection are not simple. For example, Zies, Allen and Merwin treated a lump of bornite with a  $2\frac{1}{2}$  per cent  $H_2SO_4$  solution at  $200^\circ$  for two days and found it coated with covellite and chalcocite and replaced along cracks by chalcopyrite. They discuss the results as follows:

The acid first attacked the surface of the bornite, altering it to cupric and cuprous sulphides, ferrous sulphate and hydrogen sulphide being formed at the same time. The interior thus became protected from the direct action of the relatively strong acid and the small amount of acid which did penetrate was greatly weakened by reacting with the bornite. Under these conditions we have found that ferrous sulphate, cupric or cuprous sulphide, and hydrogen sulphide will react and form chalcopyrite. The most likely place for the chalcopyrite to develop will be, of course, along the lines of fracture and cleavage, since they afford to the acid the readiest means of ingress.

The most interesting factor of mechanical protection in this bornite experiment is what we have already called area of exposure. Despite chemical differences among the sulphides, this may be the dominating factor. For example, a sulphide, no matter how resistant, lying on the wall of a major channel in which air and water circulate freely, will become thoroughly oxidized. Or, the protection by inaccessibility may be superadded to chemical stability, as when pyrite is surrounded by chalcocite which, chemically more attackable, is occupying the very position of greatest favorability to change.

Or, the sulphide may be buried in fine-grained quartz. Such quartz, cryptocrystalline or chalcedonic, and dark gray because of a fine pepper of disseminated pyrite, galena or sphalerite, may outcrop at the very surface, though sulphide less protected is deeply oxidized nearby.

Again, the sulphide may be buried in kaolin which, if bulky enough, will never dry out and will, therefore, permit but slow access of oxygen.

In mechanical protection, much depends on the porosity of the oxidation product. Calcite dissolves and makes openings. Chalcocite changes to a pseudomorphic "limonite" sponge, far more porous than itself and, during oxidation, leaving a good pathway to the sulphide nucleus within. Galena, on the other hand, may make a swelling oxidation product which encases the galena nucleus more and more tightly, preserving it to the outcrop.

Much depends also on the climate. In the semi-arid Southwest, pure chalcocite grains, "sifting upward" through the mixed zone at the top of the sulphide, may remain too dry to oxidize, and survive until they emerge at the surface. Or, held in capillary openings, and thus isolated from other sulphides, they may be protected from outside sources of SO<sub>3</sub> and, therefore, though supplied with abundant oxygen, may yet remain unoxidized.

A carbonate gangue, by generating CO<sub>2</sub>, may protect sulphide by pushing back oxygen from it. Thus is sometimes explained the simultaneous formation of "limonite" as an outer rind and of chalcocite or covellite as an inner rind in the same specimen surrounding a residual nucleus of sphalerite.

At Tintic (Utah), in aggregated deposits in limestone, oxidation descends to the water level, some 2000 feet deep, but relict sulphides are strewn abundantly between the water level and the surface. To the preservation of these sulphides, undoubtedly carbon dioxide has contributed. But it could have done so only where the sulphide was imbedded in a medium such as kaolin, permitting only slow access of air; and in and near large openings such as caves and "water courses," the supply of air would greatly exceed that of carbon dioxide and would sweep it away.

So much for the general factors of preservation. Let us now correlate these factors with field evidence.

Morse, from specimens which he collected at Triunfo (Lower California), an arid locality, describes the sequence from sulphide to surface as follows: The sulphide, which occurs in steep quartz veins, is unoxidized at the depth of 50 feet. Below that depth it consists of quartz, pyrite, arsenopyrite, galena, sphalerite carrying dots of chalcopyrite arranged along the crystal directions, and a number of complex lead-antimony sulphides. It carries 0.2 per cent copper and important quantities both of silver and gold.

Above the depth of 50 feet, the minerals begin to be oxidized but in a definite order upward. Arsenopyrite goes to a yellow pulverulent arsenic mineral, and the lead-antimony sulphides to oxidized lead-antimony compounds not yet identified. Next above, sphalerite disappears, and the copper in its included chalcopyrite is gathered together and precipitated as covellite on galena and the residual leadantimony sulphides. Its zinc is in part lost and in part precipitated in an arsenical or antimonial compound. the sulphide nucleus becomes smaller the covellite continues to envelop it as a thickening rind until, with the disappearance of the nucleus, it survives as a solid nodule in the midst of the oxidized lead masses. The pyrite is still largely untouched. After the sulphides other than covellite and pyrite have been destroyed, pyrite begins to oxidize with increased rapidity. In the outcrops, all of the iron, lead, gold, silver and copper are retained and most of the arsenic and antimony, about one-tenth of the zinc and very little of the sulphur. The lead and zinc lie in the arsenical and antimonial compounds mentioned above. The iron exists as "limonite" and scorodite but, also, as residual sulphide, for about one-tenth the total amount of pyrite has survived. The copper exists as covellite and nearly all the covellite has survived. No important volume change is proved between sulphide and capping and no important residual or other enrichment is known to have taken place.

Field evidence of contrasted behavior among the sulphides was found by Knopf in the Rochester district, where a very fine-grained dissemination of pyrite, sphalerite, galena, tetrahedrate and chalcopyrite in a "chalcedenoid" matrix showed replacement of sphalerite by covellite and argentite. "... the pyrite was practically immune to the reactions that produced the argentite and covellite and this immunity is to be attributed to the fact that the easily attackable sphalerite was present in abundance. It

Oxi	idation zoning at Triunfo, Lower California (Morse)										
Surface	Covellite Limonite Scorodite Residual pyrite Lead and zinc arsenic and antimony compounds Gold and silver										
ouriace -	Covellite Pyrite, diminishing upward Lead and zinc arsenic and antimony compounds Gold and silver										
	Pyrite Covellite Oxidized arsenic and antimony minerals (including some lead and zinc-arsenic and antimony compounds) Gold and silver										
KO fact doon	Pyrite Galena and covellite Part of the sphalerite Oxidized arsenic minerals including some zinc-arsenic compound Oxidized lead-antimony compounds										
50 feet deep -	Pyrite Arsenopyrite Sphalerite with dots of chalcopyrite Galena Complex lead-antimony sulphides Gold Silver										

is clearly manifest that the sphalerite reacted much more readily to form argentite and covellite than any other hypogene sulphide in the ore, except possibly galena." Even in ore deeply iron-stained, pyrite, argentite and covellite survived.

Additional evidence is given by Lindgren and Loughlin, who found in Tintic (Utah) that in small amounts chalcocite and covellite were formed during the oxidation of enargite and famatinite and that they develop contemporaneously with the arsenates of copper. But, they say, "It is generally known that enargite is one of the minerals most resistant to

oxidation. Its presence seems to some extent to protect pyrite which is preserved in many places where one would expect it to have been oxidized."

Finally, there is one more striking example, which was contributed orally by W. R. Brown. In Ely (Nevada) during the shut-down lasting one year the chalcocite ore became so oxidized that, to the depth of one steam shovel cut (50 feet), 15 per cent of its copper became soluble. The chalcopyrite ore, however, remained unaffected. This example illustrates not only the relative inertness of chalcopyrite, but also the great speed with which chalcocite can be broken down under favorable conditions.

The field examples are numerous, but there is no need to multiply them, for they show little beyond that already given.

From all these considerations, four important rules emerge: (1) sphalerite, if iron bearing, is destroyed in advance of chalcocite, bornite, chalcopyrite, covellite or pyrite; (2) the sulphides, other than sphalerite, to some extent often survive in the metore as relict grains; (3) pyrite survives in especial abundance; (4) but with mechanical protection, any sulphide whatever may be preserved; and (5) in the surface layer even the sulphide so preserved may be destroyed.

With the aid of these rules, relict sulphide is useful at the present time as a guide in certain places such as Triunfo, and, with metores sampled for relict sulphide, the subject promises to develop rules even more specific than those now available. It is worth energetic study both in prospect examinations and in work toward the development of outcrop technique.

## CHAPTER X

## THE IRON PRECIPITATES

This paper, in the midst of much general matter, has yielded glimpses here and there of the actual task of reconstructing particular kinds of sulphide. Its various subjects, chemistry, water level, gangue, voids, content of heavy metals and relict sulphide, have approached more and more nearly to that task. Of all these subjects, relict sulphide is indeed the most direct. Because, however, the iron precipitates are more abundant, more constant in their behavior, and better understood, their study, which constitutes the subject of this and of the following two chapters, is the most useful of all and yields the most abundant and comprehensive information.

The difficulty of the task of reconstruction, as has already been shown, varies with the position of the particular outcrop in the series of metores. With present knowledge, the degree of assurance in this task at the aggregated end of that series is almost nil; it increases with approach toward the disseminated end. In other words, the assurance is least when the iron is exported from the specimen altogether, or when it floods the matrix; it is greater when the iron moves out merely into halos and borders contiguous to cavities representing grains or veinlets of sulphide; it is greatest when the iron remains in place.

These principles cause the metores to be classified by their ease of reconstruction, as follows:

Iron indigenous
Pseudomorphic
Clinging to walls of voids
Iron transported
Remaining contiguous in
halos and borders

Little change in volume or in iron content between ore and metore: the common case in capping: reconstruction feasible

Flooding the matrix

Iron exported

Larger change in volume and in iron content between ore and metore: the common case in gossan: reconstruction more difficult

We are now brought to an essential step in understanding the reconstruction of metore. Not only is the reconstruction easiest at the disseminated end of the series where the iron most strongly tends to remain in place, but it is among the metores found toward this end that the presence of copper makes the most manifest difference in the behavior of the iron. For, the greater the proportion of copper in the sulphide, the greater will be the pseudomorphism of the iron precipitates.

## DISTINCTION BETWEEN INDIGENOUS AND TRANSPORTED LIMONITE

The distinction between indigenous and transported "limonite" is of prime importance, for, as was suggested above, indigenous "limonite" is one of the principal evidences of former sulphide copper.

With experience, this distinction is not difficult. The indigenous "limonite," of course, reproduces the exact pattern of the sulphide: it assumes the same veinlet and speck shapes and is similarly related to quartz-lined microvugs and to sericitic rock. The result of oxidation may be the mere substitution of "limonite" for sulphide. The observer acquainted with the features of the sulphide ore instantly detects any change of aspect resulting from iron transportation. Moreover, while indigenous "limonite" is unlikely to be diluted with kaolin, sericite or quartz, transported "limonite" often makes a "fog" of microscopic spherulites, discs, or plates in feldspar, sericite or kaolin.

Another means of distinction is a contrast in texture and form. Transported "limonite" tends to a variety of kinds—halos, paints, crusts, veinlets, botryoidal, clayey, earthy,

rigid, sub-metallic, iridescent. Indigenous "limonite," on the other hand, is far simpler and is of only three principal kinds: (1) a weak, irregularly and finely porous body termed "relief limonite," which suggests the former presence of chalcocite; (2) a boxwork, coarse or fine, making a porous pseudomorph after the sulphide, which means chalcopyrite or bornite; and (3) rigid linings, often fibrous and botryoidal, or finely nodular and sub-metallic, clinging to the inside surfaces of voids from which sulphides have been removed and in certain ore bodies meaning a mixture of pyrite and chalcocite. These, and other varieties, will be later taken up in detail.

In the distinction of indigenous from transported "limonite," it is to be noted that transported "limonite" is far more conspicuous than indigenous and that its proportion tends, therefore, to be exaggerated. This rule, however, does not apply invariably to all the minerals, for jarosite, being light colored, might be overlooked when mixed with kaolin or sericite.

#### THE MINERALOGY OF THE IRON PRECIPITATES

The iron minerals precipitated in the metores might be expected to differ with the presence or absence of copper in the ore. This consideration brings us to their mineralogy.

The common iron precipitates in metores are goethite, hematite, jarosite, siderite and nontronite.

The following text book "series of hydrated iron oxides" suggested by variation in water content is shown by Posnjak and Merwin not to exist.

Turgite	$\text{Fe}_2\text{O}_3\cdot\frac{1}{2}\text{H}_2\text{O}$
Goethite	$Fe_2O_3 \cdot 1H_2O$
Hydrogoethite	Fe <sub>2</sub> O <sub>3</sub> ·4H <sub>2</sub> O
Limonite	Fe <sub>2</sub> O <sub>3</sub> ·§H <sub>2</sub> O
Xanthosiderite	
Limnite	

The actual minerals of the supposed series are only: (1) hematite  $(Fe_2O_3)$ ; and (2) goethite and lepidocrocite  $(Fe_2O_3 \cdot H_2O)$ . Hematite, fibrous, with adsorbed and capillary water, is turgite. Goethite is also often fibrous, with adsorbed and capillary water. Limonite is not a mineral species and is used in this book with quotation marks to designate fine-grained, undetermined iron precipitates.

Jarosite is the double basic ferric sulphate,  $K_2O \cdot 3Fe_2O_3 \cdot 4SO_3 \cdot 6H_2O$ . Nontronite is a hydrous ferric silicate, whose composition is thought to be  $Fe_2O_3 \cdot 3SiO_2 \cdot 3H_2O$ . It is soft, clay-like, sometimes fibrous, sometimes micaceous, and much too dark for kaolin. Its optical properties are not entirely certain. Siderite is ferrous carbonate,  $FeCO_3$ .

All these minerals as occurring in metores are fine-grained, intermixed with impurities, and difficult to study. Their determination has been and is being pursued by Tunell on specimens from Morenci (Arizona), Bingham (Utah) and Tyrone (New Mexico). But, though in most of the outcrop study (except that by Tunell) the intermingled iron precipitates have not been separated but have been put together under the name, "limonite;" and though the distinctions found significant of the kinds of sulphide have been based on macroscopic texture and distribution; nevertheless, mineralogical rules are now developing.

Thus, in the three localities which he studied, Tunell has found that the iron precipitates consist largely of definitely crystalline hematite, goethite and jarosite. Though a certain amount of each mineral occurs in such confused aggregates that he cannot prove that it is not amorphous, he believes that this, also, is largely crystalline, and, with the help of color distinctions has been able to identify practically all of the iron-bearing minerals and to establish very rough proportions for the three districts (see table 7).

The identification of these minerals by Tunell was accomplished by indices of refraction, optical orientation and color

in grains of measured thickness. The procedure in a particular case is illustrated by the following statement:

The material in question was a solid brown veinlet 0.1 mm. thick in capping from Morenci. A thin section of this veinlet shows that it is composed of a yellowish-brown translucent mineral with irregular lenses of a deep red to opaque mineral in some places along the middle of the veinlet and in some along the sides. In the powder from the veinlet, tiny pieces of light brown transparent crust with a botryoidal surface were observed. The crust was attached to bits of opaque material. In parallel light between crossed nicols, a stationary black cross was visible in each lobe of the crust which showed that the crust was made up of radiating fibers perpendicular to the botryoidal surface. The radii of the crust lobes were about 0.01 mm. long. The crust had a bright yellow polarization color. A number of particles of the powder were immersed in a molten solution of piperine and iodides of antimony and arsenic, the

TABLE 7

Percentages of total oxidized iron contained in the various minerals
in the cappings

	MORENCE	BINGHAM	TYBONE
Hematite	15 per cent	Very little 66 per cent 33 per cent	Much Much Little

solution was quenched and the embedded grains were observed under the microscope. By comparison of the indices of refraction of the particles with the known indices of the piperine and iodides glass, the indices of the fibers of the particles were found to be  $2.04 \pm 0.04$  and  $2.07 \pm 0.04$ . The fibers had a positive optical elongation.

The sign of the elongation was tested by means of the Becke line in sectors of the crust lobes having very small angles but showing definitely an arm of the black cross which remained parallel to the polarizer while the sectors were rotated from the position in which one side was parallel to the polarizer to that in which the other side was parallel to the polarizer. The elongation was determined also by means of the Berek compensator.

After identifying the minerals of these three districts, Tunell correlated them with immediately underlying sulphides and found the following conditions to mean a high ratio of copper to iron in the sulphides: (1) a high ratio of indigenous to transported iron; (2) a high ratio of hematite to goethite; (3) a high ratio of hematite plus goethite to jarosite. An abundance of jarosite he correlated with a high ratio of pyrite to copper-bearing sulphide.

The first of these ratios as an indication of copper is accordant with field evidence gathered, not only in these particular places, but in all the districts so far studied. The second and third ratios, outside of the three districts in which Tunell worked, have been studied in the field only in a rough way by the mineral color, but the field information available suggests, though it does not prove, their general soundness.

The meaning of jarosite as suggested both by the field evidence and by the chemical considerations is important, and warrants, therefore, a close examination of the field occurrence. Jarosite, a double basic ferric sulphate, is especially abundant in the iron precipitates formed in limestone or siderite. It is also rather common in open spaces such as cracks, vugs or microvugs, even in non-carbonate gangue, and it occurs as tiny crystals peppered through sericite and kaolin. In general, it is produced more commonly in arid than in humid regions.

Butler has found jarosite most abundantly in limestone country. Hewett has encountered it (with sufficient plumbojarosite to make ore) in Southern Nevada (an arid region) both in limestone and in other rock such as rhyolite. In veins in this same part of Nevada, he saw zones of double basic ferric sulphates succeeded toward the surface by zones of "limonite." And, 25 miles southeast from Las Vegas (Nevada), he found "cauliflowers" of jarosite, 10 to 20 feet across, outcropping in the midst of alum-bearing, chalky, decomposed rock. These "cauliflowers" he considers a surface concentration by evaporation.

Lindgren describes basic copper and ferric sulphates in Chuquicamata (Chile) as persisting to the surface. Significant conditions are extreme aridity and low sulphur content in the ore. In the outcrops of the Eagle prospect (Plumas County, Calif.) and the Dyke prospect (Lemhi County, Idaho), jarosite and iron oxides replace siderite in a mixture of siderite, calcite, pyrite and chalcopyrite disseminated sparsely in schist. In mine workings, basic sulphates occur in complex mixtures of sulphates which come out on the walls as efflorescences. (See p. 59.)

As is illustrated above, jarosite occurs under a variety of conditions. According to the Posnjak-Merwin conclusions, the precipitation or persistence of jarosite would be improbable either in very acid or in very dilute solutions. The proved favorability of aridity, which makes the solutions concentrated, and of limestone, which brings the acidity down, is, then, harmonious with laboratory experiment. As was already noted, it seems improbable that jarosite would precipitate or long persist below water level.

Jarosite is usually not pseudomorphic after sulphide, but transported. It occurs in the aggregated more abundantly than in the disseminated part of the metore series and, therefore, in metores that are difficult to interpret in terms of the sulphide. Excepting in the sense that abundant transportation of iron usually means abundant pyrite, it is not significant of any particular kind of sulphide.

Nontronite, which, as was stated on page 68, is being found in increasing abundance, has been but little studied. It may prove to mean abundant pyrite. But there is reason, in some cases, to suspect that it is a product of plain weathering and has no necessary meaning in terms of sulphide. It constitutes clayey masses which, when dried, develop shrinkage cracks and it may in some cases be an early stage in the formation of other, more rigid iron minerals.

Siderite is most commonly hypogene. Usually that which

is supergene is distinguishable by greater porosity and greater purity. But the test of purity is not always applicable, for, in Bisbee, the supergene siderite boxwork formed below oxidizing pyritic bodies in limestone (see p. 54), carries as much as 5 per cent manganese.

The principal supergene form of siderite is the boxwork just now mentioned; another supposed form is sub-microscopic inclusions in the iron oxide minerals (see Posnjak and Merwin). Though both these forms indicate low acidity at the place of precipitation, their iron is known in all observed cases to have been derived from a highly pyritic source and to have travelled sufficiently far to reach a neutralizing environment such as limestone. In disseminated ores, siderite has not been found to have importance. In aggregated limestone ores, however, the boxwork is common and it there constitutes a reversed gossan, indicating mineralized ground above and not below.

The work so far accomplished suggests that the mineralogy may contain whole new regions of information on the problems of outcrops. And, even should it not result in the rigid use of certain oxidized iron minerals as diagnostic of certain sulphides, the determination of those minerals, and their relations to the gangue must be learned in great detail for their bearing on the processes of oxidation.

## SHRINKAGE TEXTURES OF THE INDIGENOUS IRON PRECIPITATES

It is of interest to inquire into the shrinkage involved in the oxidation of various sulphides. We shall calculate this shrinkage theoretically for two sets of cases: (1) where conditions are such that all the iron remains in place despite any excess of S above that needed to carry off the copper; and (2) where conditions are such that the excess S carries away a part of the iron. For purposes of discussion, we shall assume that the copper departs as CuSO<sub>4</sub> before the iron begins to depart, and that the iron deposits as Fe<sub>2</sub>O<sub>3</sub>·H<sub>2</sub>O from a solution of Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·

The results of the calculations are shown in table 8. In this table where there are two original sulphides, the volume

FABLE 8

			TABLE 8						
	other	IF AL	L Fe REMAINS	if part of Fe i excess S as					
ORIGINAL MINERAL	Volume ratio of pyrite to other mineral	Volume ratio of pseudo- morph to original	Porosity	Volume ratio of pseudomorph to original mineral	Perceity				
FeS <sub>2</sub>		0.93	Slightly porous	All departs					
Fe <sub>7</sub> S <sub>8</sub>		1.08	Dense	0.26	Very porous				
$2 \text{FeS}_2$ $1 \text{Cu}_2 \text{S}$	1.6	0.57	Porous	All departs					
$\frac{1}{2}$ FeS <sub>2</sub> Cu <sub>2</sub> S	0.4	0.26	Very porous	None departs					
$ \begin{array}{c} 5\text{FeS}_2\\ 1\text{Cu}_5\text{FeS}_4 \end{array}\right\} $	1.25	0.615	Porous	All departs					
$\frac{1}{2}$ FeS <sub>2</sub> $\left.\right\}$	0.125	0.31	Very porous	None departs					
Cu <sub>5</sub> FeS <sub>4</sub>		0.23	Very porous	None departs					
$1 \text{FeS}_2$ $1 \text{CuFeS}_2$	0.55	0.66	Porous	All departs					
CuFeS <sub>2</sub>		0.51	Porous	0.16	Very porous				
$\left. \begin{array}{c} {\rm 3FeS_2} \\ {\rm 1FeCO_3} \end{array} \right\} \ldots \ldots$	2.40	0.88	Slightly porous	All departs					
FeCO <sub>3</sub>		0.74	Porous	None departs					
$K_2O \cdot 3Fe_2O_3 \cdot$		0.45	-	0.00					
4SO <sub>3</sub> ·6H <sub>2</sub> O		0.43	Porous	0.28	Very porous				

ratios, pyrite other original mineral, are so selected that, according to the assumptions regarding the solutions, either (1) all the copper departs and all the irons remains; or (2) all the copper and all the iron depart.

The assumptions are only partly justified; for the iron would depart in a solution of  $Fe_2(SO_4)_3$  only within a limited range of concentration. (See Posnjak and Merwin.) Again, not all the iron would come under the rules established by the Posnjak-Merwin experiments, for a portion of it would remain ferrous. Still again, the copper would introduce complications not yet covered by the experiments. But, even though the assumptions were correct, impurities such as silica and water would change the volume of the precipitate and, therefore, its porosity. For example, a gel is sometimes formed which has a molecular ratio,  $H_2O$  to  $Fe_2O_3$ , of many to 1, and which greatly exceeds the volume of the original mineral.

Yet, despite these complications, experience with large numbers of specimens of known derivation shows porosities very often lying between those indicated in the two porosity columns of the table and suggests, therefore, that natural conditions may commonly fall within a range making the used assumptions somewhat close to the actual conditions. As was stated on page 36, the complications of the presence of ferrous iron, for example, do not seem serious, for in disseminated ores thorough oxidation has been found to be a reasonable postulate. The fact is established by experience that the "limonite" textures vary with the sulphides in a way so marked that they can be used in identification.

### THE COLORS OF THE IRON PRECIPITATES

From the beginning of the study of outcrops, there was noticed a variation of color with the sulphides from which the iron precipitate was derived. In extreme cases, this was so marked as to serve for the selection of good ground. In view of the complicated factors which in general contribute to the production of a given color, such a result is contrary to expectation.

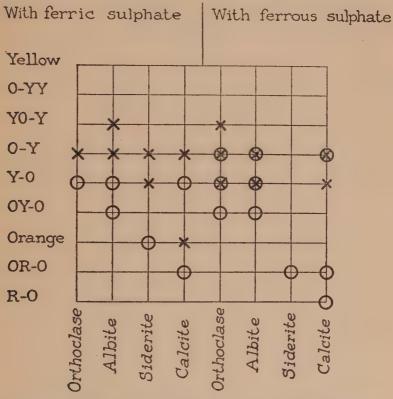
The most important factor in color is the character of the iron mineral produced by oxidation. Posnjak and Merwin state that the powders of the various minerals have colors as follows:

Hematite.																								
Turgite	 						 				 								bı	ig	ht	r	ed	į
Goethite.	 		• •				 	 		 ٠	 	• •	 d	ul	1	0	Γį	3.1	ng	е	ye	11	ow	7
Jarosite					 	 	 				 								. 3	rel	lo	w	ish	1

But there are factors other than mineralogy which affect color, namely, the fineness of division, the degree of packing, and the impurities. Pulverization multiplies the surfaces of reflection and has the effect of increasing admixtures of white light. Moreover, by differential absorptions of color. there are actual spectrum changes with changes in fineness of division. For example, hematite, massive, is black: ground in a mortar, it becomes deep red; ground still further, it acquires a touch of orange. Fine porosity has the same effect as pulverization. Impurities might have an important effect. A little adsorbed copper or manganese, because these make strong colors, might dominate the color result. Quartz, kaolin and sericite dilute the "limonite" with white. Water produces little difference, though if it fills capillary openings it darkens the shade by decreasing the reflection of white light.

Because, then, the iron minerals vary in their purity and in their fineness of division and degree of packing together, sometimes being earthy, sometimes massive, sometimes painted on surfaces, sometimes strewn in fine particles through gangue, the color of the same mineral varies in shade and hue. These complications do, in fact, in many cases, make the color too variable to be of value unless it is carefully analyzed. But there are certain cases having a narrow range of conditions, in which the color has less variety and has been used as diagnostic of kinds of sulphide. Such cases are especially found in disseminated metores where the iron is indigenous.

To investigate the influence of copper on color, Morse made iron precipitates by boiling solutions of ferric and of ferrous sulphate, with various "precipitants," both with and without added copper. The colors were as follows:



Y, yellow; O, orange R, red; O-Y, orange-yellow; O, with copper; X, without copper. (Colors by comparison with Ridgway charts.)

It will be noted that the precipitates from the copperbearing solutions tend toward the orange and red side, while those from solutions lacking copper tend toward yellow. The obvious explanation is an impurity of copper. But none of the precipitates contain as much as 1 per cent copper, and several, starting with copper in solution and lying on the orange and red side, contain not even a trace. The explanation, then, is that the copper seems in some way to have affected the nature of the precipitated mineral, the size of its grain, or the degree of its packing, so as to cause some peculiarity of color in the precipitates.

Indeed, there is a similar color tendency noticed in the field. Blanchard, from studies in Silverbell (Arizona), Santa Rita (New Mexico), Tyrone (New Mexico), Morenci (Arizona), Plumas Co. (California), and various places in Sonora and British Columbia, concludes as follows:

In the field, the "limonites" over known disseminated ore usually have a deep maroon (dull reddish brown) to seal brown color. I know of no important deposit where these colors are not present in the capping, although they must, in some instances, be looked for closely. At a distance of a few hundred feet, the brown tinge often fails to show and a deep reddish appearance is presented.

The bright red "limonites," called "brick red" by us, have nowhere been observed except over pyritic areas where the copper content of the enriched zone, as a whole, averaged much less than 0.5 per cent copper. Not all the low grade pyritic areas are brick red but the field evidence is that brick red "limonite" has nowhere been found over actual ore ground.

Tunell, in field and microscopic investigation, gets similar results. He writes (unpublished work):

The outcrops above the high grade Racket orebody (Tyrone, New Mexico) and the high grade Harrison orebody (Morenci, Arizona), in which the oxidation products of the sulphides are mainly indigenous hematite with some transported hematite and some indigenous and transported goethite, have a deep maroon color with an undertone of seal brown due to goethite.

The cappings above the pyritic waste on the Continental Divide ridge northwest of the Racket orebody and above the pyritic waste on the upper levels of the Utah Copper Mine at Bingham (Utah), in which the iron oxide is mainly transported goethite, have a yellowish brown color.

Although the writer has studied no cappings with a general brick red color, he has collected samples from the capping of the Clay orebody (Morenci, Arizona) and from Tyrone, which contained an unusually large amount of transported hematite, and these appeared brick red.

The writer believes that the explanation of the various colors of the capping above disseminated ore and pyritic waste lies in the following facts: hand specimens containing much transported hematite are brick red; much indigenous hematite, maroon; much indigenous goethite, deep brown; much transported goethite, yellowish-brown; and much transported jarosite, yellow.

A good example of such color differences is that between the "north hill" of the Miami mine (Arizona), which covers a pyritic, slightly enriched orebody of about 1 per cent copper, and an area farther south in that mine in which lies a 2.5 per cent chalcocite orebody, thoroughly enriched and low in pyrite. The "north hill" is conspicuously reddish and highly colored, from paint on numerous joints. The outcrop farther south is much paler: its "limonite" lies in inconspicuous, maroon-colored specks and veinlets pseudomorphic after sulphides, and, although it carries only traces of copper, the color of the "limonite" from copper-bearing sulphide is highly characteristic.

These studies indicate that color does, in fact, vary in some degree with former copper content. They will be mainly useful, however, not for general application, but for suggesting what to look for in a given place. The way to use color is to see it accurately and then generalize over the smallest possible area, establishing, in the peculiar combination there found of kaolin, quartz, and sericite with "limonite," the peculiar color which means one kind of sulphide rather than another.

### WEATHERING OF FEMIC ROCK MINERALS

In concluding this chapter and before taking up the kinds of iron precipitates signifying particular sulphides, it is desirable to consider the weathering of femic rock minerals.

Iron minerals of disseminated metores are very sparingly derived from this source, not only in the surface layer, but also at the top of the sulphide. They are here mentioned mainly for the confusion which they might create in the aggregated metores.

The principal iron-bearing rock minerals found in aggregated copper ores are biotite, hornblende, pyroxene, chlorite, garnet, epidote, serpentine, magnetite and hematite. Of the silicates, those richest in iron, of course, make the most serious problem in outcrop interpretation, for they not only yield the most abundant "limonite," but they weather the most easily. For example, thuringite, an iron-rich chlorite, was found by Emmons and Larsen in Creede (Colorado) to have been replaced by "limonite" to the depth of 500 feet below the surface.

This is a more than usually troublesome case, for, according to the description, no thuringite whatever comes through to the surface. In all other cases, however, of which the writer knows, although the "limonite" from femic minerals has no characteristic qualities, it shows gradations, even at the surface, into remnants of unweathered minerals. Of these remnants, those from garnet, hematite and magnetite are especially abundant.

To summarize: In disseminated metores, the femic rock minerals yield "limonite" only in unimportant quantities. In aggregated metores, they yield it more abundantly, but study will reveal actual gradations and prevent confusion with "limonite" of sulphide origin.

## CHAPTER XI

## SIGNIFICANT KINDS OF IRON PRECIPITATES

### GENERAL

All the conceptions regarding outcrops began with a set of simple observations that particular "kinds of limonite" in the metore correspond to definite kinds of sulphide in the ore. These observations were made in many districts of the Southwest and adjoining regions. They constituted a part of the task naturally imposed on the field engineer during the examination of prospects and mines and were based on the collection and study of numerous suites of specimens whose sulphide derivation was known.

But the full use of the empirical rules thus derived required the development of ideas of process; for it is only when we have thought the subject through its various aspects that we can become best equipped for its application in the field. It was this necessity that led us into the consideration of chemistry, water level, and various other subjects which have no immediate bearing on the search for ore.

After all, however, it is the original simple observations, thus broadened and refined, which constitute our principal tools. It is to the use of these tools that we shall devote the remaining part of this book.

## Descriptive terms

The iron precipitates possess numerous physical qualities and the tendency has arisen for different observers to select different sets of those qualities for emphasis in description. Our purpose demands that we select and emphasize those sets which we know to vary with the kind of sulphide.

In order, therefore, to simplify and standardize descriptions, the following list of terms is provided. Such definitions as are needed are given in the glossary.

List of descriptive terms for limonite

1. Indigenous

Contiguous Transported

Exotic

Imported

Coextensive with place of sulphide

Clinging to inside of wall of

voided cavity

Making halos or borders to emptied cavity or crack

Controlled by crack

Flooding

Stain (fog)

Painted

Peppered

Discrete specks

Cementing conglomerate

Impure

2. Red Orange {

3. Dull

Vitreous

Resinous

Pitch

Metallic

Submetallic

4. Uneven

Conchoidal

Hackly

Splintery

5. Earthy

Chalky

Powdery

Pulverulent

Plastic

Coherent

Friable Rigid

6. Dense

Absorbing water

Submicroscopic With pores Microscopic Macroscopic

Sponge Boxwork

Tufa-like

Septum

Mesh

Shrinkage gash

Shrinkage crack

Crackled

Riddled with holes

Granular

7. Fibrous

Botryoidal

Spherulitic

Amorphous

Banded

Platy

Scaly

Crusted

Nested

Stalactitic

Reniform

Columnar

Ragged

Crinkled

Clotted

Nodular

8. Crystalline

Fibrous

Amorphous

9. Cubic pseudomorph Irregular pseudomorph

10. Jaspery "limonite"

Limonitic jasper Relief "limonite"

## The limonite scale

In the classification of "limonite," several well defined kinds were readily separated by physical, macroscopic qualities. These kinds make a scale, within the range of disseminated ores, varying from one end, at which copperbearing sulphides are abundant, to the other end at which pyrite is abundant. The steps of that scale are:

- 1. "Relief" "limonite"
- 2. "Limonite" pitch
- 3. Fine "limonite" boxwork
- 4. Coarse "limonite" boxwork
- 5. Minutely nodular crusts lining voids left by sulphide
- 6. Halos and borders contiguous to voids left by sulphide
- Halos and borders attached to voids left by sulphide, but separated from them by unstained zones
- 8. "Limonite" in various forms unattached to voids left by sulphide, such as that flooding the matrix.

This scale accords with increasing transportation of iron. For instance, while nearly pure chalcocite often makes a fine sponge of "relief" "limonite" exactly pseudomorphic after the sulphide, a mixture of chalcocite and pyrite may leave a cavity lined with "limonite" which, on its inner side, is minutely nodular; and pure pyrite may vacate its cavity entirely, leaving merely halos or flooding the matrix throughout. Because, however, these kinds are mere stopping places in a continuous series, gradations must be expected, and no one specimen will be found exclusively exhibiting any one kind.

Now, in the simplest case, the oxidation occurs grain by grain so that the several tiny "limonite" bodies can be separated into those from pyrite and those from a mixture of pyrite with chalcocite. This is the result when, in its narrowest sense, we have "cloister" oxidation (see p. 61). But in Morenci (Arizona), Bingham (Utah), and Tyrone (New Mexico), Tunell (unpublished work) found conditions described as follows:

In a thin section of enriched ore taken at random, there are perhaps 75 grains of pyrite with very thin chalcocite rims and perhaps 50 smaller grains of solid chalcocite. In a thin section of capping a foot or two away, all the cavity linings have about equal thickness and all either lack halos or have halos of equal thickness. There is no difference between the individual linings derived from pyrite grains and those derived from chalcocite. If the general ratio of pyrite to chalcocite in the given small area were different, all of the tiny bodies of iron oxide would be of a different type. The conclusion is that the oxidation took place by areas and not by grains.

This means that, in these specimens, we did not have "cloister" oxidation in its narrowest sense. But it means, also, not that the "limonite" left behind is the same for a whole group of pyrite grains as for a whole group of chalcocite grains, but that all the grains within the limits of the thin section participate in the effect of the mixture and yield a "limonite" characteristic of such a mixture.

Even in these specimens, then, the kind of "limonite" is correlated with the amount of sulphide copper. This is true in general. But, to thrust into a district rules of correlation found applicable outside, while neglecting to establish the habits which could be determined in the very ground in question, is poor practice. The kinds of "limonite" in general are useful merely to suggest what to look for: and, as in every other part of the outcrop problem, generalizations must be put to use in prospecting through discerning study at the place where they are going to be applied.

#### DESCRIPTIONS

Relief limonite correlated with chalcocite or covellite accompanied by minor pyrite

"Relief" "limonite" exactly repeats the arrangement of the former sulphide grains and veinlets. Each tiny body, therefore, signifies a sulphide body of equal size.

But the "limonite" is far less compact than the sulphide

was. It is minutely craggy, cavernous, porous and, because of the tenuity of its numerous interlocked, skeletal parts, very weak. The crags stand up like the objects in a stereoscopic field. When a specimen is freshly broken, tiny sponges of it rise above the general surface. In outcrops, because of its weakness, it is readily whipped out by the weather. It may even be shaken out from the broken surfaces of hand specimens. Even, then, where existing in very small amount, its presence is highly significant.

The streak color is deep orange or deep reddish orange (maroon). The external color is much darker, merging into black.

The texture of relief "limonite," though not well shown in photographs, is suggested in plate XV. One of the stages between relief "limonite" and that derived from a mixture richer in pyrite is shown in plate XIX A. Here botryoidal cavity linings carry rounded knobs with stalactite-like projections pointing inward: they are all composed of radiating fibers and are compacted to the walls instead of making a porous filling of the whole cavity.

There exist gradations on the one hand from the true relief "limonite" to that making cavity linings; and on the other hand to an ill-defined, clay-like "limonite" which was sometimes observed to be a first stage in the oxidation of sulphides very rich in chalcocite, though also observed to be derived from pyrite.

Through the correlation of relief "limonite" with actual sulphide, it is traced to chalcocite or covellite with minor amounts of pyrite. There is danger of confusion with the fine boxwork derived from chalcopyrite and bornite, but this boxwork can usually be distinguished by a lighter orange color and by the angularity and greater uniformity of its cells. There is no danger, however, of confusion with the products of pyrite, for pyrite yields nothing at all resembling this kind of "limonite."

Examples. Although relief "limonite" is a well-defined kind of material, it, of course, varies in quantity and in its associations with other forms of "limonite." Its typical occurrence is illustrated by a specimen from Ray (Arizona).

This is composed of sericite schist with schistosity obscured by recrystallization into smaller plates; spotted with blebs of "limonite" reaching a diameter of 5 mm.; and traversed by a crack carrying "limonite" paint.

The bleb "limonite" is largely of the relief variety and is of a strong, dark reddish-orange color: this "limonite" is constantly grading within the blebs to the firmer variety which adheres as crusts to the walls of cavities. The firmer "limonite" means the presence of a little more pyrite than that required by relief "limonite" alone.

The "limonite" of the crack is transported and would, therefore, seem incompatible with the rest of the specimen, for, while the bleb-filling indicates chalcocite-rich sulphide, the crack-filling indicates sulphide rich in pyrite. The inconsistency, however, is only apparent, for the material in the crack is the imported paint which, becoming well removed from its sulphide source, penetrates cracks in all parts of the metore and is, therefore, significant of sulphide beyond the limits of the given sample.

The specimen is easy to read. According to the habits of the district, it means abundant large blebs of fairly pure chalcocite making an ore between 5 and 10 per cent copper.

While this specimen shows "limonite" from chalcocite associated with pyrite slightly more abundant than that usual in ores producing relief "limonite," another specimen to be described below comes from almost pure chalcocite.

This is from the Copper Basin mine (Nevada). The rock is a fine-grained sandstone with kaolin between the grains of sand. It is slightly stained here and there with a thin yellow fog and laced with a "limonite" network which goes throughout the specimen, leaving free from "limonite" areas 2 mm. to 1 cm. in diameter.

For the most part, the network consists of aggregates of "limonite" grains constantly gathering close together, then scattering out in a train of tiny specks and sometimes losing all semblance of linearity and constituting a mere pepper spread through the rock matrix.

The "limonite" is all indigenous. It is of a clear, strong reddish-orange color, has the relief character well developed and is extremely weak. It is actually a dried-out clay broken into tiny blocks which have developed curved drying cracks between minute, nested shells. Only if it were drier and harder, would it constitute relief "limonite" of the ordinary kind.

This specimen, excepting in the thin, yellow fog, shows no iron beyond the limits of the former sulphide grains. By the habit of this district, it means almost complete chalcocite enrichment in the preexisting sulphide. There is something characteristic even in the color. The specimen may be interpreted as representing an ore of about 5 per cent copper.

## Limonite pitch correlated with bornite and chalcopyrite accompanied by minor pyrite

"Limonite" pitch, because it is a temporary stage, seldom surviving long enough to reach the outcrop, is less useful than the other forms described. It is mentioned in this place on account of its derivation from sulphides having about the same ratio of copper to sulphur and iron as exists in the sulphides which weather to relief "limonite;" and because, therefore, it comes toward that end of the scale where the transportation of iron is negligible.

"Limonite" pitch resembles and may grade into copper pitch. It is a poorly defined material consisting, not only of iron oxides, but also of varying quantities of water, silica, copper, etc. Sometimes it has no copper even when adjacent to chalcopyrite. The external color is very dark brown

and sometimes almost black. The streak is light brown. It is compact and has a pitchy lustre.

The pitch replaces bornite or chalcopyrite pseudomorphically, and without development of porosity, around the peripheries of grains, along the borders of veinlets, and in laceworks of tiny veinlets separating residual sulphide islands. (See plate XVI.)

Wherever the pitch is found, sulphide is either adjacent or not more than a few centimeters distant. On the other hand, the pitch can be seen altering to the fine "limonite" boxwork next to be described.

From the pitch itself, there is no way of telling whether it is derived from bornite or from chalcopyrite. But it is distinguishable from that which so often replaces pyrite cubes in limestone for this has a less pitchy luster.

Example. A specimen from Mizpah (Nevada) illustrates well the occurrence and the temporary nature of the "limonite" pitch. In this specimen, a white quartz vein, 3 cm. thick carries masses of chalcopyrite partly oxidized. The chalcopyrite is minutely threaded by pitch, leaving angular chalcopyrite islands, sometimes so small as to be dust-like, and especially abundant in medial major areas. Outside these major areas are borders of solid pitch, and outside these borders is fine, sharply cellular "limonite" boxwork of a bright orange color, laced across by thin pitch stringers and studded here and there by pitch residuals.

The chalcopyrite grades into the pitch and the pitch into the cellular "limonite."

Fine limonite boxwork correlated with bornite and chalcopyrite accompanied by minor pyrite

As was shown in the last example, the fine boxwork may be derived from the pitch. Whether or not the boxwork may come directly from sulphide is not known, but, when we have seen the boxwork wrapped about a sulphide grain, we have time after time found it separated from the grain by intervening pitch.

The fine boxwork occurs in indigenous blebs, often as mere specks peppered through the matrix but sometimes growing to a diameter of several centimeters. Each bleb consists of a sponge with fine angular cells whose walls are of paper-like thinness. Here and there occur major, thicker walls, persisting for 1 or 2 cm. past many cells, and a system of coarser boxes is in this way packed with a sponge of the fine boxwork cells. Both the thicker and the thinner walls are composed of "limonite" with an impurity of fine-grained quartz or radially extinguishing chalcedony. (See plate XVII.)

The walls are thin compared with the cell diameters and despite its rigidity the mass is weak. When the sulphide was chalcopyrite, the cells tend to be empty giving a porosity of 75 to 90 per cent. But when the sulphide was bornite, they tend to be thickly coated or even filled with earthy, orange-colored "limonite," which may obscure the cellularity. The external color of the boxwork itself is dark orange and the streak color light orange.

The origin of this cellularity, and of the segregation in this peculiar structure, are questions which have not been answered. Polygonal shrinkage of the brittle pitch, or even of the sulphide itself, may be a part of the process, but that is, of course, not a complete explanation of so strange a process: it would not accord, for example, with the occurrence in some of the cells of curved shells surrounding residuals of clayey "limonite."

Whether or not the boxwork, once formed, persists without further change is also not known; but it is surmised that acid released late in the oxidation may sometimes change it to the more compact botryoidal cavity linings.

The fine boxwork differs from anything we have seen coming from pyrite, for the porous "limonites" from pyrite are

"sponges" with irregularly rounded, rather than angular, openings; they are coarser and have the botryoidal glossy surfaces which result from the presence of abundant acid; and their cell walls, in proportion, are thicker.

There is danger, when abundant earthy "limonite" is present, that, if care is not taken, the boxwork will be confused with the fluffy "limonite" which replaces calcite and siderite.

The fine boxwork has been found as a derivative only of chalcopyrite and bornite and has been proved one of the tangible guides to areas of ground containing those minerals.

Example. Following is described a specimen from the Pride mine (Sierra Co., Calif.), showing the stages of formation of the fine boxwork. In a coarsely crystallized quartz vein with a 10 cm. bleb of "limonite" peppered with numerous tiny chalcopyrite residuals, the "limonite" grades from (1) a part consisting of a firm, coarse boxwork whose septa, somewhat pitchy, enclose cells up to 2 mm. diameter filled with chalcopyrite islands, to (2) a part in which the chalcopyrite islands are somewhat replaced by "limonite" much more finely cellular and with webs of paper-like thinness, fragile, readily breaking into tiny scales, and dark orange in color, to (3) a part in which the chalcopyrite islands are wholly gone except for some extremely tiny specks, the pitchy septa occurring only very occasionally, and the bulk of the mass being composed of the finely cellular orange "limonite" above mentioned. The ill-defined materials. such as earthy "limonite," so commonly found, are here absent.

This finely cellular "limonite" shows no sign of the textures, such as fine nodularity, which are derived from ores with abundant pyrite. The wide distribution of the tiny chalcopyrite residuals is extraordinary and is the kind of result that might come from shrinkage during oxidation, allowing oxygen to reach many parts of the specimen at once. There is

some suggestion, also, that the last of the chalcopyrite was more resistant than the first; systematic variations in solution concentration or the disjunction of electric couples may have effected this result.

This specimen is, of course, one of the many in which we have seen such peculiarities and it is described to show how intriguing the problems are and how much there is still to be learned.

# Coarse limonite boxwork correlated with mixtures of chalcopyrite and pyrite

The "limonite" here considered is derived from a mixture of sulphides having a somewhat larger proportion of pyrite than that of the three kinds discussed above. It occurs in blebs one to many centimeters in diameter and therefore larger than those of the fine boxwork. It has been observed to favor metores in which coarse blebs and nodules of chalcopyrite have been oxidized in quartz veins or in fissured ground in which quartz is the predominant gangue.

Each bleb or nodule consists of a coarse angular boxwork, made up of "limonite" or jaspery "limonite" in thin, intersecting walls one millimeter to one centimeter apart. These walls are rigid, in part continuous in straight lines past several cells, and these lines are sometimes repeated in parallel orientation throughout the specimen.

The external color is very dark; the streak color is dull reddish-orange. The cells may be empty and in that case it has been found that the pyrite is approaching the chalcopyrite in abundance. Or, they may contain variable amounts of orange-colored pulverulent "limonite" and this has been found to indicate purer chalcopyrite.

The development of the boxwork was studied under the microscope in the various stages of oxidation, and, although there is no assurance that what was seen is a general rule, it is sufficiently usual to warrant description. In the pri-

mary sulphide, minute, glassy silica veinlets are seen ramifying the nodular mass. They either follow fractures with angular intersections within the sulphide nodule or branch around individual sulphide grains. They are most numerous at the outer edges of the sulphide nodule, adjacent to the quartz gangue, and within that nodule in the areas immediately surrounding included quartz grains.

As oxidation proceeds, the veinlets advance into the purer sulphide until a connected boxwork spreads throughout the sulphide mass with sulphide residuals filling the intervening spaces. But these extensions of the veinlets consist, not of glassy silica, but of jaspery "limonite" or, in some cases, of "limonite" without any admixture of silica whatever. Moreover, the supergene material not only makes extensions of the hypogene silica veinlets but also coats or even replaces them.

The extension of the veinlets proceeds at the expense of chalcopyrite. As oxidation goes farther, the sulphide residuals within the boxwork become more and more completely altered, at last leaving the cells already described either coated with pulverulent "limonite" or completely empty.

The coarse boxwork, so far as we have seen, is derived directly from the sulphide and not through the pitch stage and is not proved to come from any sulphide other than chalcopyrite or a mixture of chalcopyrite and pyrite.

Example. Transitional stages in the formation of the coarse boxwork can be seen in a specimen from the Pride mine (Sierra County, Calif.).

This shows a vein of coarse quartz with "limonite" of three kinds: (1) a varnish on quartz; (2) a coarse, sharp, rigid boxwork with mesh as wide as 5 mm., and with individual walls persistent past many cells and meeting almost rectangularly; walls brittle, rich in silica; external color black, and streak dark orange-red; and (3) a boxwork grading into the last and, though similar to it in structure, dif-

ferent in composition, for it consists of a light orange, clay-like material. Both kinds of boxwork hold within their cells loose, angular, residual islands of chalcopyrite up to 2 mm. in diameter.

The varnish indicates that at least a little iron departed from the place of the sulphide. Even this could have come from chalcopyrite.

The clay-like boxwork is the kind we have come to regard as "temporary." The rigid boxwork resembles that which we have found elsewhere coming from chalcopyrite and whether or not it is a hardened phase of the other has not been determined.

By some means, the chalcopyrite was crackled on a formal pattern. Oxidation proceeded along the cracks and those cracks defined the boxwork as it now exists. So long as chalcopyrite is oxidizing, a part of the "limonite" in this specimen evidently does not harden. Furthermore, indigenous "limonite" precipitates only in the earlier stages of oxidation, and, once the boxwork is completed the chalcopyrite islands go out entirely, leaving cavities. The porosity, calculated in this material by a specific gravity determination and an analysis, was 80 per cent—slightly below that given in the calculated figures based on the assumption that one molecule of chalcopyrite yields one-sixth molecule of goethite. (See p. 110.)

The lack of the pulverulent "limonite," common when pyrite is absent, has not been explained.

# Botryoidal cavity linings correlated with mixtures of chalcocite and pyrite

This is the kind of "limonite" mentioned on page 121 as a stage into which relief "limonite" passes by gradations as the proportions of pyrite to chalcocite increase. Its distribution is similar to that of the relief "limonite;" that is to say, it repeats the arrangement of the former sulphide grains and veinlets.

But, instead of being minutely craggy and porous like that which comes from purer chalcocite, this "limonite" is compacted to the wall of the void and its surface is submetallic and minutely nodular or botryoidal. By the microscope it is shown to be fibrous. Its external color is dark brown or black and its streak color reddish or orange. In some cases, the void inside the crust is filled with jarosite.

These minutely nodular crusts have not been found coming from bornite or chalcopyrite or mixtures of these minerals with pyrite. Nor have they been found coming from pure pyrite, except in cases where this lies close to chalcocite grains which have evidently participated in the reaction. But our failure to find these crusts coming from these other minerals does not prove that they will never be found when additional districts are studied, since no reason appears why these other sulphides should not produce this effect.

Nevertheless, the botryoidal cavity lining has been found in whole districts to mean nothing but mixtures of chalcocite and pyrite and has proved a useful guide to exploration.

Examples showing gradations between these crusts and "relief" "limonite" are numerous: one of them was described on page 121. Gradations in the other direction are shown in plates XXI and XXII.

Halos and borders correlated with mixtures of sulphides rich in pyrite

The cases described above are all of indigenous "limonite." Those still to be described are all of transported "limonite" and they successively exhibit increasing distances of transportation from the sulphide source and have been found to correspond to increasing proportions of pyrite to the copper-bearing sulphides.

The first kind of transported "limonite" to be considered is that still contiguous to the place of its sulphide source in the form of halos and borders. These halos and borders are 1 mm. to 1 cm. in diameter. They are common in a kaolinic or sericitic matrix where they may vary from a mere "fog" or stain to almost pure "limonite." In a quartz matrix, they are absent, for the "limonite" there either fails altogether to precipitate or makes merely a paint along cracks.

The halos or borders consist of discrete microscopic particles—discs and sperulites of goethite and hematite—all peppered in varying states of aggregation through the matrix close to the place of the former sulphide. Or, in part, these minerals make ill-defined, iron-stained patches in the surrounding gangue.

The halos or borders have not been observed to be made by pure chalcocite, bornite, chalcopyrite, sphalerite or femic rock minerals. Their usefulness lies in the fact that we have found them in several districts associated with the botryoidal cavity linings described above, and with assurance indicating there a chalcocite-pyrite ore.

But, in other districts, they have been found to come from pure pyrite. This means conditions in the gangue causing contiguous instead of remote precipitation, despite the abundance of the acid liberated by the sulphide. Fortunately, the similarity of the products of pure pyrite to those of sulphide mixtures has proved less confusing than would be expected; for work in the field definitely establishes which of the two it means. Although, then, halos and borders have no such universal significance as relief "limonite" and the fine and coarse boxworks, they become equally specific in connection with a knowedge of the local habits.

Plates V, XXI, XXII, and XXIII illustrate the halos and borders, both as seen in the field and in the thin section.

# Halos and borders correlated with pyrite

In the cases described immediately above, the acid generated by the sulphides is sufficient to carry the iron out of the cavity but not sufficient to make it proceed far into the

gangue. As the pyrite of the mixture increases and with it the acidity, a condition will be reached at which, although the iron proceeds farther into the gangue, it still precipitates in a definite relation to its source. And, indeed, in the field we often find that the iron derived from veinlets and disseminated grains of pure pyrite comes down in halos and borders lying at a little distance from their sources and separated from them by unstrained zones. (See Plate VII A and B.)

These halos and borders resemble in texture and mineralogy those more closely adhering to the place of the sulphides. Unlike these others, however, which sometimes go with hard linings in the cavities which they surround, these have their cavities empty or merely "painted" on the inside with iron oxide.

This is the limit of iron migration which permits us still to read the history of the individual grain or veinlet. In this case, there has been enough acid to clean out the void and to clean out a narrow zone adjacent to it. But there has not been enough to move the iron wholly across the ground intervening between this grain or veinlet and the next. A slight change of condition involving a larger migration of iron will produce halos attached, not to single grains, but to groups of them. A still further change will cause the flooding of the matrix and will bring conditions to the stage at which interpretation, by present knowledge, becomes speculative.

Limonite in various forms flooding the matrix correlated with pyrite

We have come, in the scale of "limonites," to the end of those definitely indicating kinds of sulphide. In the "limonite" now to be described, the travel of the iron is so great that its relation to its sulphide source is obscured. This result is marked in gossans rather than in cappings, that is, in ores richer in sulphide than those which are termed disseminated. But it is found also in cappings from disseminated ore rich in pyrite and, in smaller quantity, in cappings from disseminated ore of the copper-rich type. Even in the last case, specimens flooded with "limonite" are found intermixed with the specimens showing indigenous "limonite."

Now, the fact of flooding—as contrasted with the retention of the iron in indigenous or contiguous form or as crusts, halos, and borders—is the important matter. For flooding, regardless of the form taken, indicates that the iron has so extended its area of reaction that it can no longer be used as significant of the sulphide of that particular specimen. Some iron is certain, in fact, to have been imported into the specimen and some to have escaped down to the ground water.

Furthermore, once the iron goes "out of bounds," the forms taken by the precipitate vary, not with the character of the sulphide from which their iron came, but rather with that of the matrix in which they are precipitated. Of course, other pertinent factors are present, but the matrix seems to dominate. For instance, in an inert gangue, such as quartz, iron once dissolved does not commonly precipitate at all, but moves on, leaving a quartz sponge or sand behind. In a sericitic, feldspathic or kaolinic gangue, on the other hand, it tends to become widely strewn as paint, spherulites and disks. In such matrix, the neutralization is slow enough to permit penetration of iron some distance into the neutralizing medium. But in limestone, the travel comes to an end as soon as the solution comes in contact with the rock and only along cracks insulated by inert mineral, such as "limonite," alunite, or kaolin, can it proceed farther.

These various forms of transported "limonite," as was stated above, are by no means absent even in disseminated, copper-rich ores. In ores of a given grade, there is, indeed,

no universal proportion between the number of flooded specimens and those having indigenous "limonite." But in the given district or smaller area, such a proportion can be definitely established by experience and made to serve as a definite guide.

The distinctions between indigenous and transported "limonites" have already been to some extent discussed. It is now necessary to take up in detail some additional forms of transported "limonite" in order that these distinctions may be made more complete.

Fluffy limonite replacing carbonate. One of the transported forms which tends to be confusing is fluffy "limonite." This is shown by the hand lens to consist of grains loosely piled together. It is earthy, and has the relief and incoherence of powdered sugar. Its color is dull yellow. Often, included within it, there is jarosite. Sometimes there are relics of rhombohedral structure consisting in the imperfect alignment of grains parallel to the crystal directions of the replaced carbonate.

Fluffy "limonite" commonly replaces limestone about or below oxidized massive sulphide deposits. It constitutes a gossan which points inward or upward toward the ore. Often, it forms alternating crusts with dense "limonite" or with a rigid, fine sponge of "limonite;" and near the advancing front of replacement, these may be found surrounding spherical residuals of limestone, a few inches or feet in diameter. (See plate X.) The alternation is not understood, though at times we have believed that it might accord with seasonal variations of water supply.

Similar "limonite" now and then replaces pyrite, but in these cases no relics of rhombohedral structure have been found. Here the oxidation could have been effected by waters carrying an excess of neutralizer such as CaHCO<sub>3</sub>, for where we have found such "limonite" replacing pyrite, we have found also conditions which could have rendered the water lime-bearing.

The fluffy "limonite" is not easy to distinguish, without practice, from the fine boxwork of chalcopyrite or bornite origin when the cells of that boxwork contain earthy "limonite." The difficulty is increased by the original inclusion within the replaced carbonate of specks and veinlets of chalcopyrite, for, in that case, one is masked by the other. utility of the distinction is made evident by our experience at the Eagle prospect (Plumas County, Calif.). showed areas of inviting size with abundant veinlets, tiny lenses and specks of copper-bearing pulverulent "limonite" in schist and was regarded as promising. Exploration was carried on in tunnels. At a depth of 50 feet, the "limonite" was found changing to veinlets and specks of siderite and calcite of identical size and shape, including smaller veinlets and specks of chalcopyrite and pyrite, the material containing only about 0.5 per cent copper.

When the sulphide was reached in this prospect and its subordinate amount was observed, we undertook to determine why we had mistaken "limonite" replacing carbonates for "limonite" replacing chalcopyrite. It was in the course of this study that we first recognized the significance of the fluffy "limonite." We, furthermore, found it rich in jarosite and this, as was later realized, is another characteristic of "limonite" replacing carbonate. Had these features been realized in advance, they would have saved us the exploration.

Example: With this principle established, it is remarkable how vivid a story a single sample can tell. A random specimen from an unexplored part of the Zonia prospect (Yavapai County, Ariz.) is a good instance of what is meant. consists of quartz-feldspar porphyry, kaolinized and cut by a very irregular network of dark yellow "limonite" veinlets. The "limonite" of the irregular network covers about onehalf the specimen. Though at first glance it resembles iron stain soaked into feldspar, in reality it is fluffy "limonite"

carrying here and there spacks of hard, dark "limonite."

It gives no copper flame.

The fluffy character suggests precipitation by veinlets of carbonate equal in size to those of the "limonite." There is no reason to suppose the existence of any sulphide except pyrite and the dark specks are interpreted as meaning grains of pyrite whose iron was prevented by the carbonate from migrating. Indeed, a few small pyrite grains remain. Furthermore, the specimen is shown by analysis still to carry about 4 per cent of CaCO<sub>3</sub>. There is furnished, therefore, a positive argument that this material never carried copper, for, with this excess of "active neutralizer," a good part of any copper ever possessed by it would assuredly have been retained.

Fine limonite sponge replacing carbonate. In the description of fluffy "limonite" were mentioned alternating crusts of that "limonite" with a fine "limonite" sponge.

This sponge will now be described. It consists of a fabric made up of strings and clots of goethite, hematite, and quartz granules enclosing minute openings. Often the fabric is invaded by large calcite crystals, each of which grew by filling a multitude of pores.

The fine "limonite" sponge is a common result of the replacement of limestone in the walls of solution caves. Like the fluffy "limonite," it is a gossan pointing upward or inward to the former place of sulphide in which pyrite was predominant. The intergrown calcite crystals, being of later origin, may be taken as evidence of a change in the solutions from a condition rich in iron and sulphuric acid to one rich in lime and carbonic acid. This change may be supposed to occur with the oxidation of the pyrite, and the calcite may be taken to signalize the completion of that oxidation.

The fine "limonite" sponge differs from the fluffy "limonite" in being coherent and rigid, though it may be brittle. It differs from the fine boxwork after chalcopyrite in having

rounded rather than angular cells and in having the cell walls relatively thick instead of thin and sharp. Furthermore, instead of a light orange, it usually has a dark orange streak.

Coarse limonite sponge replacing kaolin. Of the sponges replacing kaolin, the best marked is coarse, and made up of clusters and jumbles of cubic or irregular cells up to 5 mm. in diameter, with walls of hard, dark, rigid "limonite" rich in impurities of quartz and kaolin. Sometimes the cells are sprinkled on the inside with jarosite crystals.

The clusters and jumbles of cells are identical in pattern to clusters and jumbles of pyrite cubes and grains found in feldspathic or sericitic matrix. The oxidation has resulted in the total transportation of the iron and its partial precipitation in the immediately adjacent wall. A part of the iron has doubtless traveled farther and been lost from the specimen.

A similar but finer sponge is found in curved crusts surrounding residual cores of massive pyrite. Though a large part of the iron has been lost, these crusts, in part replacing pyrite and in part replacing the intermixed matrix, serve to prove that the gossan has not collapsed during or since oxidation. Even after the pyrite core has entirely disappeared their origin is readily deduced.

Limonite clay replacing kaolin. Another form of "limonite" replacing kaolin is "limonite" clay. It is met in kaolinic rock which has been traversed by strong acid- and ironbearing waters derived from oxidizing sulphide. Their relation to the sulphide resembles that of the large scale halos of fluffy "limonite" that replaces limestone, except that, the replaced material being kaolin, the iron travels farther from its source before being precipitated.

This "limonite" clay, or "iron clay" as it is sometimes called, is of varying composition, having large admixtures of water, kaolin and colloidal silica. When this material dries,

it cracks. But it dries more slowly than the more rigid, porous kinds of "limonite" and tends to protect sulphide which it happens to envelop.

This clay is not found in cappings and, even in gossans where it occurs, it is lost in the outcrop. It is discussed here because the suggestion cannot be avoided that this is a temporary form through which, particularly in gossans, other forms pass and from which, as time proceeds, they are evolved.

Jaspery limonite replacing kaolin. Of composition roughly resembling that of the "limonite" clay last described, but less hydrous, is the so-called jaspery "limonite" which is found in gossans as a replacement of kaolin. The history of this "limonite" is revealed by an examination of the successive stages of flooding.

Incipient flooding is shown in halos and borders (see p. 130). In a further stage, sericitic, kaolinic rock, originally peppered with pyrite grains and cut by pyrite veinlets, becomes soaked throughout by "limonite" or acquires a widespread "limonite" fog (see p. 133). This has moved out along cracks and crept through the uncracked rock in capillary openings. By minor volume adjustments, cracks open and become painted or crusted with botryoidal "limonite" and jarosite, or solidly filled from wall to wall as though the growth of the mineral had forced the walls apart.

Then, in a more advanced stage, the fog is so thick that the individual granules of "limonite" become contiguous and the kaolin becomes totally replaced by a dense, jasper-like body composed of a very fine-grained "limonite" intermixed with microcrystalline or radially extinguishing silica. When the jasper-like body is rich in silica, we call it "limonitie" jasper; when it is rich in "limonite," we call it jaspery "limonite."

In no case has quartzite or other non-aluminous rock been found undergoing this change. Quartz veinlets remain unreplaced. Quartz phenocrysts of a replaced rhyolite may survive, studding a 40 per cent iron ore. The quartz residuals often occur as curved streams of shattered, angular fragments coursing through the dense jaspery matrix and slightly removed from each other as though by the growth of the matrix.

The production of jaspery "limonite" involves an enrichment in iron. But enrichment in one place means impover-ishment in another and, except where the gangue is appropriate, impoverishment of the body as a whole, instead of enrichment, occurs. Thus, bodies of jaspery "limonite" and leached siliceous sponges or sands lie side by side.

In the interpretation of outcrops, jaspery "limonite" is a noteworthy material, because its resistance to erosion makes it emerge in exaggerated proportion at the surface; and because the flooding and destruction of texture render it impossible to read closely in terms of sulphide. It is often confused with hypogene jasperoid and much money has been spent in the exploration of both under a vague impression regarding their relations to ore. The first step in their intelligent interpretation is their distinction from each other and this is not a difficult task.

When this distinction is made and when flinty outcrops have been identified as jaspery "limonite," it is realized that they indicate merely the replacement of kaolinic ground by solutions, rich in acid and iron, that came from a sulphide rich in pyrite; and it is also realized that the metore which is likely to tell a story concerning the presence or absence of copper is softer and tends to lie covered with detritus. Holes dug around the eminent knobs of jaspery "limonite," and around any hard outcrop, have proved to be very informing.

Limonite in open spaces. The forms in which "limonite" precipitates in the extreme cases of transportation are hard, rigid, crusted, banded, botryoidal and stalactitic. These, of

course, are commonly found in gossans. Their peculiarities are due to the fact that they are largely open space fillings. They are characterized by druses, by medial spaces between crusts, by fine banding, and by coarse, radial, mammillary aggregations. The open spaces may be the actual places of the removed ore minerals, as in the case of the tiny, hard crusts lining sulphide cavities. Or they may be cracks formed above the place of removal but filled from sulphide still higher up, as in slumped ground above oxidized ore in Bisbee.

In any one specimen, there may be difficulty in determining whether the iron of a given "limonite" crust filling a crack came wholly from another place or was in part originated at the place which it now occupies. But this leads to no important confusion, for the existence of these transported forms indicates abundant pyrite and this means that we are near that end of the metore series in which "limonite" is difficult to use as a guide to copper.

A porous, friable, coarse sponge now and then occurs with the other forms of open space "limonite." This is composed of loosely packed, rudely horizontal, thin leaves. In some cases, the leaves have separated as films at the air surface of a body of iron-bearing water and have settled under the action of gravity. In other cases, their origin is not known, but no example has been found in which the precipitation was not well removed from the sulphide source of the iron.

## Temporary forms of limonite

Before concluding the list of the kinds of "limonites" we have still to discuss the "temporary forms," such as "limonite" clay and pitch, which have been already mentioned in several places; and to indicate what we know of their transformation to more permanent forms.

The temporary forms have been found only in small

amount in the more strictly disseminated ores. In certain of the aggregated ores, they are found in or near the "mixed zone" lying immediately on the sulphide. Within a few feet upward they change to the rigid, cavernous gossan with which we are so familiar.

Looked at more closely, the temporary forms are found in spots grading on the one side into the sulphide and on the other side into one of the harder forms of "limonite." While much of the harder material has come directly from sulphide, some of it has come through this softer stage. The transition results in a striking increase in coarse porosity and this is one of the reasons why gossans are riddled with holes.

Although the study of the transitions has been made only in hand specimens, some inferences may be drawn as to the process. It is presumed that dehydration is effected both through evaporation and through crystallization; that gels dry out to loose powders; that the less inert minerals, such as jarosite, tend to be destroyed; that there may be a continuous transfer of dissolved material to places where it can deposit, such as surfaces of evaporation; that there is solution and redeposition by water in pores; and that small crystals may dissolve and big crystals build up so that the pores grow in size. But these are merely the best working hypotheses available in advance of the more critical work which results from a combination of field, microscopic and chemical studies.

Examples. A specimen of gossan from Cananea, Sonora, shows three kinds of "limonite:" (1) lemon yellow, earthy, very finely porous; (2) brownish yellow, somewhat earthy, somewhat less finely porous; (3) dark brown, dense, hard, rigid, with many holes like pin pricks and slits.

Of these "limonites," 3 occurs as borders of cracks which spread fantastically through the softer mass; 2 as borders of 3; and 1 makes up the body of the specimen. Were the softer mass whipped away, the residual skeleton would make

an eminent, carious body with "goblin shapes" resembling, on a small scale, those of some of the hard outcrops emerging at the surface.

Tunell, by microscopic study, found a clear case of the transition of jarosite to goethite in a specimen of jasperoid breccia taken a few inches above disseminated sulphide in Bingham (Utah): the breccia fragments are cemented by jarosite, so fine-grained as to be scarcely resolvable by the microscope; and the jarosite here and there seems to be replaced by brown "limonite," starting with the most faintly perceptible cloud and becoming denser near the openings. Excepting this alteration, which is small in amount, and a similar alteration in Tyrone (New Mexico), no other cases of the alteration of an iron precipitate have been observed in strictly disseminated ores. It is clear that in these deposits, the hematite and goethite, once precipitated, have not been altered at all.

#### CHAPTER XII

ESTIMATION OF THE FORMER COPPER CONTENT

According to the descriptions given above, if we avoid the flooded metores, we should often be able to estimate the former proportions between pyrite and copper-bearing sulphide from the nature of the "limonite" in the metore. For, (1) the chalcocite-pyrite ratio increases with approach to relief "limonite" and decreases with approach to compacted linings with submetallic lustre and minutely nodular surface; (2) the chalcopyrite-pyrite, or bornitepyrite ratio, increases with the proportion of pulverulent "limonite" in the cells of the boxwork, and decreases with the emptiness of the cells and with their acquisition of submetallic lustre and minute nodularity; (3) the greater the ratio of halo to compacted lining, the smaller was the ratio of chalcocite or chalcopyrite to pyrite previous to the oxidation; and (4) halos which surround inner halos of unstained ground, which in turn surround empty sulphide cavities, mean pyrite.

While these are not all the relationships which are known, they are those which have proved to be the more general and to have the more quantitative significance.

Given, then, the rough ratio between pyrite and copperbearing sulphide thus calculated, and, given the amount of sulphide-derived iron in the specimen, a rude estimation of the former copper content becomes possible.

This calculation was undertaken in samples of metore from three districts, Tyrone (New Mexico), Miami (Arizona) and Ajo (Arizona). (Morse and Locke.) The ratio among the sulphides was set according to certain chemical assumptions, but it is to be understood that these

were only surmises and that they do not actually yield information beyond that given in the descriptive matter above. Moreover, the sulphide-derived iron was assumed to be that dissolved in a few minutes by hot dilute acid. The calculations, in the particular cases chosen, came out close to the figures of the known sulphide ore occurring below, namely, 1.50 to 2 per cent copper. But, though an approximation was to be expected, the closeness of the check was accidental. And, indeed, the same experiment tried on Morenci (Arizona) samples, gave discordant results, because the sulphide-derived iron failed to dissolve readily and so failed to be readily separated from iron of other sources.

Although it is believed that such nice computations have little practical meaning because in general there is only a vague basis for them, yet, where the lineaments of the capping are extremely familiar, and where kinds of capping can be traced into kinds of sulphide, it is entirely possible to do this very thing to the extent of dividing the unexplored ground into good, fair, and poor. The visual aspects of the whole specimen are what we have to grasp. The estimations so made, for practical purposes, are sufficient, for when the local habit has been established, the designation poor ground is enough to discourage exploration and the designation good ground, to compel it. It was by such a classification that Boswell, even in one of the earlier outcrop studies, was able to separate the square mile of ground in Tyrone (New Mexico) into its more and its less favorable parts. And as time went on and more definite criteria were found in other districts, it was possible, turning back to Tyrone, to refine the earlier classification.

Any classification of ground is, of course, made up from the sum of the judgments gained from individual specimens. And it is to show how such specimens are handled and to illustrate the technique of the Tyrone work that the following are described from our collection. These are selected

as showing the usual combinations of different kinds of "limonite" within the same piece.

Plate III-A shows a sericitized, kaolinized, feldspathic porphyry with about 20 per cent of its volume consisting of dark specks up to 2 mm. in diameter, rich in "limonite." These specks are, in some cases, surrounded by pale yellowish halos. In addition to the specks and halos there are crusts of "limonite" filling thin cracks.

The specks, in many cases, are coextensive with feldspar phenocrysts and possess rectangular outlines at first erroneously suggesting derivation from pyrite crystals. They each consist, however, not of solid "limonite," but of kaolin deeply stained with dark orange "limonite;" and include a pepper of tiny, dark yellow-orange, minutely nodular crusts of "limonite" lining cavities which in some cases are cubic. The dark specks, then, represent stainings of feldspar phenocrysts from included sulphide grains. The iron remains attached to particular clusters of former sulphide grains, never going outside the limits of the feldspar crystals in which it was deposited.

A few of the specks, on the other hand, lie out in the groundmass and consist wholly of the indigenous, finely nodular "limonite" with occasional cubic outlines.

The pale, yellowish halos carry only a small proportion of the total iron. They are most developed around the larger areas of indigenous "limonite."

The crusts filling cracks resemble the linings of the tiny cavities except that their nodules are less minute. To what degree they are indigenous, is not known.

The outstanding characteristics of the specimen are: (1) the "cloister" character of the oxidation, at least in part, as evidenced by the attachment of "limonite" halos to particular grains or clusters of grains of indigenous "limonite," and consisting in the absence of flooding by "limonite" in the ground between those halos; (2) the nodularity of

the "limonite," and the cubic forms; (3) the indigenous "limonite" of the grains in the interiors of the dark specks.

In this district, in a disseminated ore with this kind of gangue, the presence of crusts of indigenous "limonite" of this sort in specks without flooding means chalcocitized ore rich in pyrite. For the presence of the "limonite" in the cavities means chalcocite, but its occurrence in crusts and failure to take the "relief" form proves an intermixture of abundant pyrite. Where, as in this specimen, the total sulphide content is indicated to have made about 10 per cent of the weight, the copper content was fairly good but not exceptionally high.

Although the specimen contains no sulphides, there is little risk in the conclusion that it represents a fairly well enriched ore, with enough chalcocite to make it run about 2 per cent copper.

Plate III-B shows a specimen similar to III-A except that it has less contiguous and more indigenous "limonite."

There is a thick, shining "limonite" paint on one side of the specimen whose nature is uncertain: it may be transported or it may be indigenous with its surface "made over" by acid or built up by transported "limonite." In either case it suggests highly pyritic material at some place outside the specimen.

The specimen represents an ore carrying about 2.5 per cent copper.

Another specimen resembes that of plate III-A except that the indigenous "limonite" is scarcer and more scattered and the transported makes much larger halos.

This means a larger proportion of pyrite to chalcocite and, inasmuch as the cavities are about the same in volume, it means a lower grade ore. On the basis of our experience in this district, the specimen is regarded as meaning a 1 to 2 per cent ore.

Incidentally, the specimen illustrates very well the facts

underlying the idea of "cloister oxidation;" for, although the iron is half transported, it is strictly limited in its distribution; there is intervening, unstained ground between the halos and only a thin, yellowish fog sweeping through part of the specimen succeeds in crossing this intervening ground. Obviously, the fact that the iron halos do not reach across from one sulphide cavity to another fails to prove that sulphuric acid and ferric sulphate did not reach across and fails to establish the process of "cloister oxidation" in the strictest sense.

Plate IV-A represents a specimen which is richer in "limonite" and has all but a very small amount of its "limonite" in the cavities formerly occupied by sulphide. This specimen corresponds to a chalcocite-pyrite ore having 2 to 5 per cent copper.

Plate IV-B represents a similar specimen with very little transported "limonite," and with the grains of sulphide as indicated by the indigenous "limonite" so close together that the ore is known to have been semi-massive.

That some pyrite was present is suggested by the fact that the "limonite" is finely nodular and has a submetallic surface. That it existed in some excess over the amount needed to furnish iron to replace the chalcocite is suggested by the presence of some halos about the indigenous grains and, in a few isolated cases, about cubic cavities.

This is regarded as having been a well-enriched, semimassive ore, with 5 to 10 per cent copper.

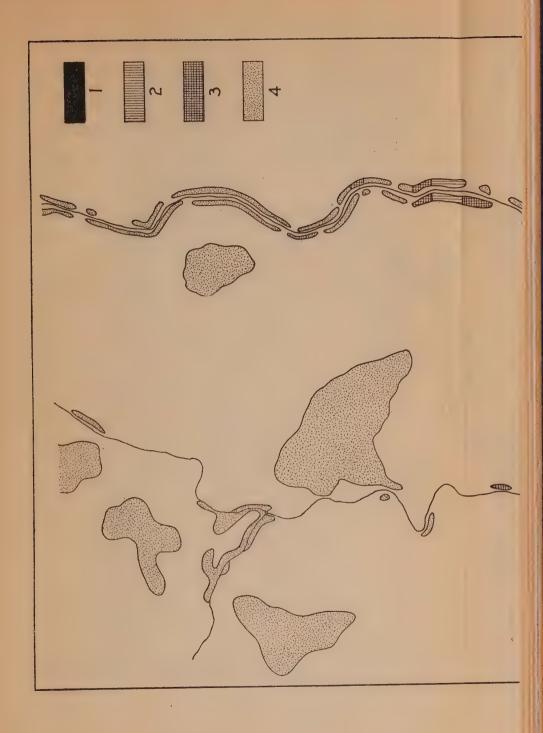
How interpretations of this sort are used to reconstruct the whole surface of a prospect is illustrated by Blanchard and Boswell's work on La Libertad prospect (Sonora). Here, as Blanchard describes it, granite gneiss is cut by several narrow rhyolite dykes, and capped at the higher elevations by scattered, small remnants of a rhyolite flow. Mineralization is of the veinlet and disseminated types, and is confined to the granite gneiss in an area 1 by 5 miles in extent. Only limited surface exploration has been done, and no sulphides have been found; but the presence of copper was proved by small occurrences of malachite and chrysocolla. The problem was to determine whether further exploration was warranted.

Since no sulphide was observed, it became necessary to judge the showings on the basis of outcrop technique developed in other districts and the doubt involved was therefore greater than in districts where transitions are actually exposed.

Eighty-five per cent of the surface was covered by 10 to 50 feet of desert debris, and outcrops of the granite gneiss were confined mostly to arroyos and scattered, low, intervening knobs; but the outcrops were well distributed over the mineralized area, and were sufficiently numerous to present a probable average of conditions.

The entire mineralized area, except a portion measuring 1200 by 1200 feet, was eliminated as being pyritic and poor in copper. The basis of elimination was: (1) the common occurrence of cubical pits in the mineralized rock; (2) the almost complete absence of indigenous "limonite" in the pits and mineralized fractures; (3) the general occurrence of transported, "painted" "limonite" adjoining the pits and mineralized fractures; (4) the fact that pits of other than cubical shape showed no difference from those which were cubical either in the type of the "limonite" within them or in the arrangement of the particles surrounding them; (5) the absence of copper.

In the 1200 by 1200-foot area, which contained all the showings of malachite and chrysocolla, many of the pits carried a maroon-colored, indigenous, slightly pulverulent, relief "limonite," closely similar in texture and occurrence to the "limonite" known to have been derived from chalcocite in districts previously studied. Since this "limonite" greatly exceeded in volume the malachite and chrysocolla,



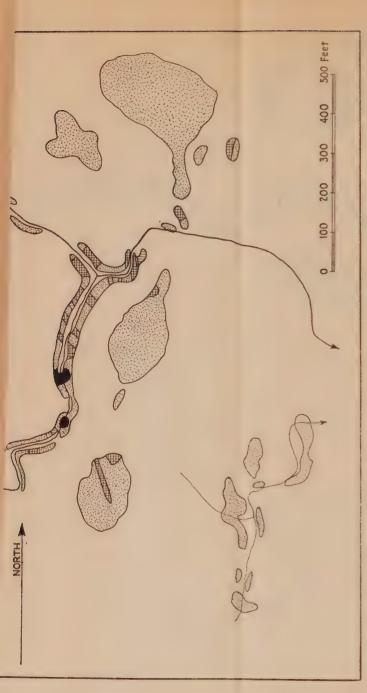


Fig. 12. Map of La Libertad prospect, Sonora, Mexico, showing all the outcrops graded according to their meaning in terms of copper. (Blanchard and Boswell.) 1, No. 1 grade of outcrop (meaning over 2 per cent copper); 2, No. 2 grade of outcrop (meaning 1 to 2 per cent copper); 3, No. 3 grade of outcrop (meaning less than 1 per cent copper); 4, No. 4 grade of outcrop (meaning essentially barren granite-gneiss).

and often occurred hundreds of feet from the copper-stained rock, the conclusion was that the amount of copper formerly in the outcrop had been much greater than that now revealed at the scattered copper-stained surface showings. Judged solely on the basis of its similarity to the "limonites" over leached chalcocite in known districts, some of this outcrop could be regarded as representing 5 to 6 per cent copper in the form of chalcocite.

It was found, however, that only a small proportion of the "limonite" in the 1200 by 1200-foot area belonged to this type. Several excellent exposures of the copper-bearing granite gneiss are afforded by the arroyos, which crosscut, at about 1000 feet apart, nearly the full width of the area, and expose a five to fifty-foot vertical section of the granite gneiss. These, together with other less continuous outcrops, show the granite gneiss to be cut by irregular, often crisscross fracture zones, ranging from 2 to 30 feet in width. The average width is about 10 feet. The lengths could not be accurately determined, but from the positions of their exposures, and the failure of their projections to intersect given outcrops, it is evident that most of the zones do not attain lengths of more than a few hundred feet. These zones are separated by stretches 50, 100 or even several hundred feet in width of slightly fractured or unfractured rock, which show only the transported, "painted" "limonite." No doubt is left that, although good outcrops. exist, they are confined to the fracture zones which are small, scattered, and discontinuous.

The following classification of outcrops was used:

- 1: Meaning ore; more than 2 per cent copper
- 2: Meaning ore of moderate grade; 1 to 2 per cent copper
- 3: Meaning material of low grade; less than 1 per cent copper
- 4: Essentially barren granite-gneiss

Since these classifications could not be checked against actual developed sulphides in the district, they are only approximate.

The percentage of outcrops of the four types was estimated as follows:

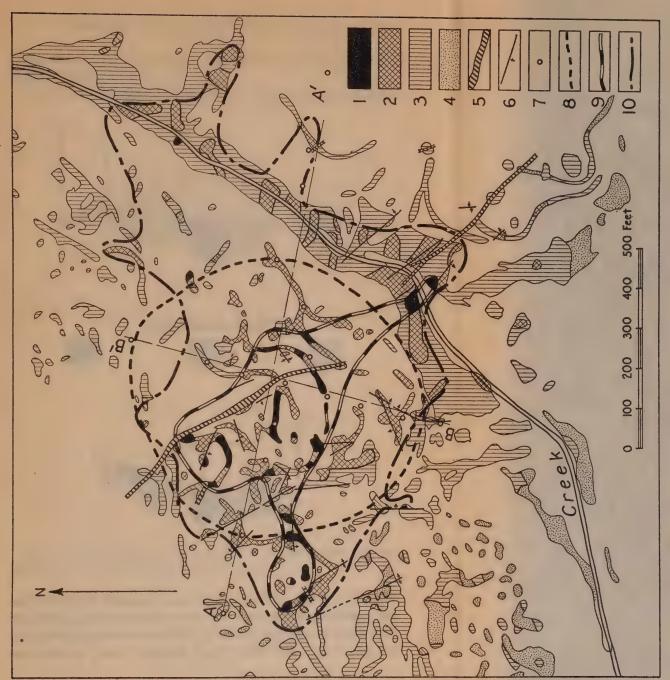
1: 0.25 per cent of the total outcrops, which constituted 15 to 20 per cent defends a 4.00 per cent being covered with alluvium.

There remained the possibility that the 1 and 2 types of outcrops, because they were softer than the 3 and 4 types, might be more deeply eroded, and therefore covered to a greater extent by alluvium. But, since the type of fracturing does not vary over the entire 1 by 5 miles area, and since the two arroyos in the 1200 by 1200-foot portion present almost unbroken cross sections of the only part of the ground that carries any evidence of copper, it is not reasonable to assume that the alluvium-covered parts carry a greater proportion of No. 1 and No. 2 material than do the actual outcrops.

Another example of similar mapping, compared however against previously existing churn drill records, is afforded by Blanchard and Boswell's study of an Arizona prospect.

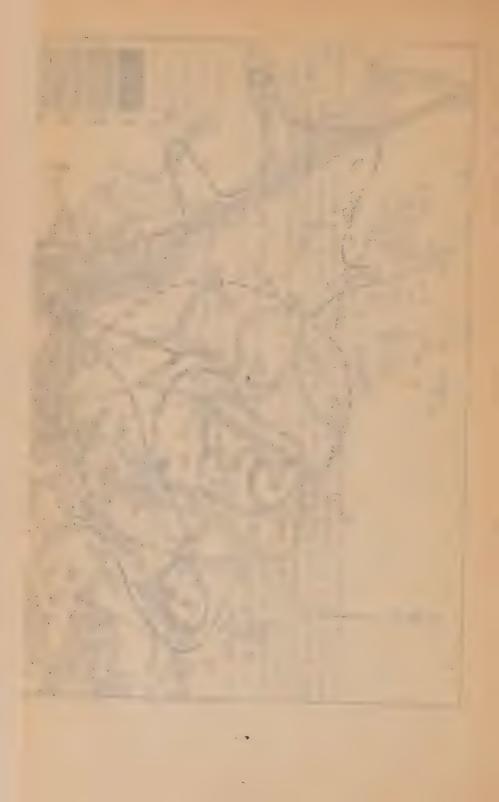
Here a body of disseminated monzonite ore had been developed by churn drill holes and by limited underground workings. The problem was to determine whether there existed a definite correspondence between the outcrops over developed ground and the material proved to lie beneath it; and, in case such correspondence existed, to apply the established criteria to other portions of the district that were suspected of containing copper orebodies, but which contained only a few scattered scout holes or remained untested.

The ore had been shown by the development to occur in lenses—from 30 to 100 feet or more in length and depth, and from 2 to 20 feet in width—crowded close together along well defined fractures which persist to the surface. Because of the lenticularity of the ore occurrence, it was obvious that a fairly large surface over proved ground must be used for judging the outcrops if a dependable average of condi-



Frg. 13. Map of an Arizona prospect showing all the outcrops graded according to their meaning in terms of copper. (Blanchard and Boswell.)

1, No. 1 grade of outcrop (meaning over 2 per cent copper); 2, No. 2 grade of outcrop (meaning 1.25 to 2 per cent copper); 3, No. 3 grade of outcrop (meaning less than 1.25 per cent copper); 4, No. 4 grade of outcrop (meaning essentially barren rock); 5, dike; 6, silica-flooded fissure; 7, churn drill hole; 8, area of the thicker ore as shown by two rows of drill holes; 9, area including the more abundant showings of the most favorable outcrops; 10, area including the more abundant showings of the moderately favorable outcrops.



tions was to be obtained. The area available measured approximately 700 by 1400 feet.

Study showed that although the outcrops are lenticular,

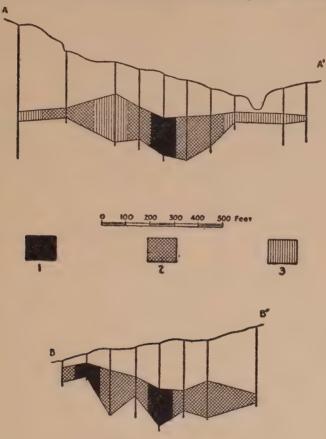


Fig. 14. Sections through area of fig. 13. 1, exceeding 2 per cent copper; 2, 1.5 to 2 per cent copper; 3, 1 to 1.5 copper.

and although in some cases lenses exist in depth that have no clearly seen equivalents at the surface, nevertheless, the areas of good outcrops have good ore beneath, the areas of moderately poor outcrops have moderately poor ore beneath, and the areas of very poor outcrops have essentially barren rock beneath.

In addition to control of the ore by the fractures, two other ore controls were found that have to be weighed with the other evidence: dikes, and fissures flooded with hypogene silica. Near these it is clear that a tendency exists for the lenses to be richer.

Although the deposits are lenticular, and although the leached outcrops by themselves do not serve as an infallible guide to any small unit area, it was possible, by giving weight to the ore controls that showed at the surface, to establish criteria for judging outlying, unprospected showings in the monzonite. These showings, on this basis, yielded no evidence of important ore.

#### CHAPTER XIII

USE OF THE RECONSTRUCTED SULPHIDE IN THE PREDICTION
OF HIDDEN SULPHIDE

This book has so far been concerned with the reconstruction of the sulphide from the metore. The reconstruction has involved two steps, namely, (1) the taking of a sample; and (2) the interpretation of that sample.

But, even with this task accurately accomplished, all we shall know will be the nature of the sulphide formerly in the metore which we can see: the surface can yield a true record only of the ore that once existed in that surface. This leaves us still the second part of the problem. Given such knowledge, how can we use it for predicting sulphide that is hidden?

As was earlier indicated, this second part of the problem resembles the search for extensions horizontally and downward from the bottom level of a mine. Though a familiar subject, it requires consideration here for the emphasis which may be put on certain peculiarities of projection when it is used for this particular purpose.

These peculiarities arise from the fact that the projection must traverse an obscure zone of metore before it can come to the sulphide which is being sought. But equally important is the fact that often when we are interpreting outcrops we have no such knowledge of the habit of the orebody as is usually available when we are working underground.

With these peculiarities, the projection becomes a problem involving four principal questions: (1) the direction in which the ore lies from the outcrop; (2) the thickness of the metore; (3) the grade of the underlying enriched sulphide as compared with that signified by the surface

showing; and (4) the thickness of the enriched sulphide. These questions we shall now consider in succession.

The miner tends to treat leached outcrop as though it accorded with sulphide vertically below and he repeatedly puts out crosscuts to "go under" some point on the surface. Except where the ore is very large and therefore easy to find, or where, though smaller, it happens to extend vertically, this practice is hazardous to a high degree. With equal reason, the crosscuts might deviate either to one side or to the other. The actual direction in which to go down from the surface is not to be decided by any such simple assumption, but is to be established by a variety of considerations.

Obviously, one of these considerations will be actual strikes and dips of orebodies as already known in underground development in the vicinity. These strikes and dips being established as closely as possible to the ground in question, it remains to be determined to what extent they apply also to that ground.

Of course, information regarding the structure of the ground itself will have been gained during the taking and study of the metore samples. The trends of the good areas, their dependence on fractures and on rock contacts, and their interruption by later faults all emerge as soon as the distinctions between good metore and poor are clearly made. This information may either confirm the habit of the vicinity or cause it to be modified.

The task of projection is most difficult when the orebodies have a spotty pattern and the sulphides lie deep. With small scattered orebodies leached to the depth of 500 feet we might laboriously determine the former quality of the now, leached metore to the half of a per cent in copper and yet, through the difficulties of projection, be unable to determine the position of sulphide ore now existing. The task of projection is simple only when the mineralized bodies are

large masses and the sulphides lie at shallow depth. Yet, in any case, intelligent study will greatly diminish the hazards of projection.

Once the direction is established, the next principal ques-

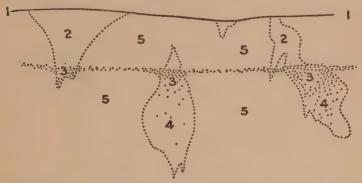


Fig. 15. Sketch cross section showing discordances between surface showings and sulphides below. 1, surface; 2, metore; 3, enriched ore; 4, protore; 5, rock inadequately mineralized to make ore.

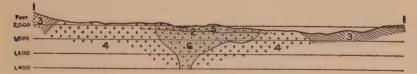


Fig. 16. Sketch showing mushrooming of ore at Ajo, Arizona, under a rhyolite roof. (Joralemon.) 1, surface; 2, water level and bottom of oxidation; 3, rhyolite; 4, pyritized monzonite; 5, oxidized ore; 6, sulphide ore (disseminated chalcopyrite and bornite with minor pyrite) of same grade as oxidized ore.

tion to be considered is the distance from the outcrop to the ore—in other words, the thickness of the metore.

Our opinion of the depth of the metore will be influenced by considerations of porosity and water level. Deep, widespread, thorough oxidation will occur in material which has zones and net works of closely spaced cracks and which is sufficiently rigid to maintain abundant openings through which water can readily move under small head. It is in such materials that water stands at a low level and hence the nature of the outcrop may be taken in some degree as suggesting the depth of the water level and the depth of the oxidation. Furthermore, there are other ways of estimating these depths, such as physiographic studies. But, in practice, this becomes vague. For, not only is the calculation of the water level from such data subject to very large error, but its relation to the bottom of the metore, as was shown in the chapter on water level, cannot be predicted in the individual case.

All this comes down to the conclusion that there is no general way of predicting the depth of oxidation, and that the evidence of a single drill hole will outweigh all the general thinking we can do on the subject. But, given outcrops which we know were derived from sulphide rich in copper, it is a simple and inexpensive procedure to establish the depth of the present sulphide by a few scout holes.

Figs. 17 and 18. Examples of actual orebodies which were poorly represented at the surface and difficult to predict; emphasizing the functions of structural geology in the interpretation of outcrops. (Observed by the writer and his associates.)

Fig. 17. A. Soft metore eroded to a bowl-like depression and hidden under deep debris. 1, surface; 2, bottom of gossan.

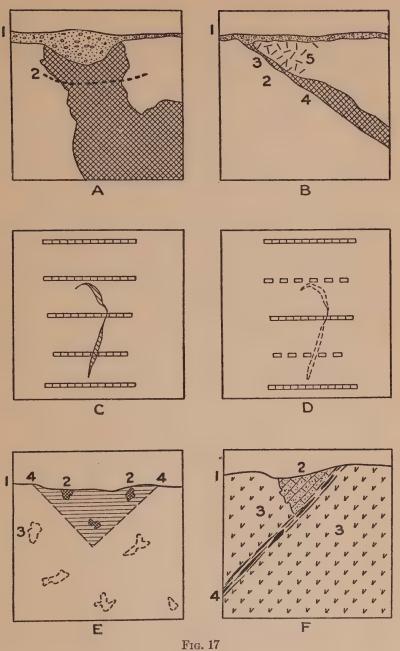
B. Soft, sandy metore, rich in gold, representing a shrunken concentrate from a much greater thickness of aggregated sulphide vein. (Kingsbury.) 1, surface; 2, bottom of weathered material; 3, sandy metore; 4, protore;  $\delta$ , caved hanging wall.

C. Plan of B as developed in trenches.

D. Plan of B showing a discouraging early stage of development in trenches.

E. Spotty orebodies apparently, but not actually, bottoming above the lower limit of exploration. 1, surface; 2, discovered ore; 3, undiscovered ore; 4, limits of exploration at a discouraging stage, diagrammatically represented.

F. Mineralized limestone block giving, at the surface, an exaggerated impression of size. 1, surface; 2, mineralized limestone block; 3, intrusive rock; 4, mineralized fissure.



**7** 

We shall now undertake the next principal question: the grade of the underlying sulphide as compared with the surface showing. Through vertical zoning, supergene or hypogene, that showing may be too good or too poor for the sulphide which structurally corresponds to it. We must not conclude, for example, that the degree of enrichment in the sulphide below is necessarily the same as that of the sulphide from which the outcrop was derived. For, where oxidation goes deep, the copper of the chalcocite has, to some extent, come out of the metore now lying above it; in other words, there was cumulative downward enrichment and, even when the sulphide below is rich in copper and the metore just above is of the most favorable quality, the outcrop itself has been found in a few cases to be merely fair. It is to be expected that further applications of the outcrop technique will define the conditions of cumulative enrichment and yield improved means for its recognition. But though, in the present state of knowledge, we can do little with this question but make surmises, the fact is that we have little reason to fear that this condition impairs our judgment in an important sense.

Fig. 18. A. A small relic of an alteration border outcropping and indicating ore below. 1, surface; 2, fault; 3, ore bed; 4, alteration border.

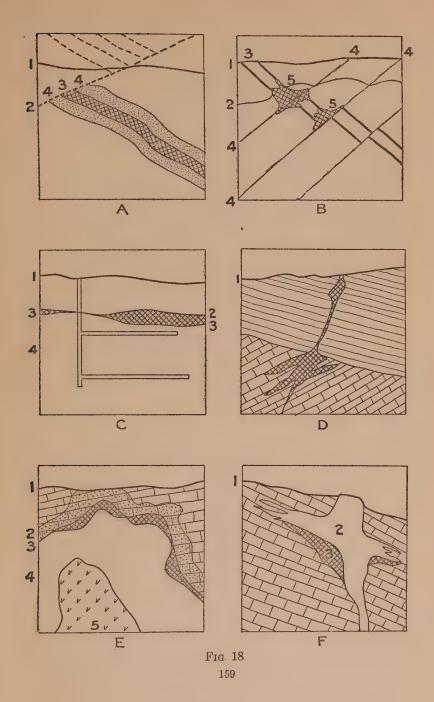
B. Separated outcrops of fractures and favorable beds pointing toward hidden favorable intersections below. ("Trough structure.") 1, surface; 2, bottom of oxidation; 3, favorable rock bed, slightly mineralized; 4, mineralized fissure; 5, chalcocite ore.

C. Rich blanket of chalcocite-silver ore underlying a favorable outcrop and overlying low grade heavy sulphide; missed by a shaft and cross cuts put too far below the bottom of oxidation; later found accidentally. 1, surface; 2, bottom of gossan; 3, chalcocite-silver ore; 4, protore.

D. Fissure ore outcropping in tuff and connecting with larger ore below in limestone. 1, surface.

E. Outcrop of "marble halo" indicating ore along a hidden "marble line." 1, surface; 2, "marble halo"; 3, ore; 4, garnet; 5, intrusive rock.

F. Outcrop of jasperoid which denotes a jasperoid enlargement making a roof for ore. 1, surface; 2, jasperoid expanding in a favorable horizon; 3, ore.



With hypogene vertical zoning, we shall have a still further complication. Obviously, if the orebodies are spotty, some may be merely the roots of something removed by erosion and some may be the upward tapering tips of larger bodies below. Or, the surface showing may be the expanded upper portion of a mushroom-like body which quickly dwindles downward. The greater part of what we know about such hypogene zoning is related to the effect of rock contacts on the mineralization and there will be no excuse for an attempt to understand a disseminated copper prospect without attention to the rock structure as shown by its environs. These questions demand a vigorous search for the alternatives of possibility which are to be tested by drilling or other exploration.

The next principal question is the thickness of the enriched ore. Deep enrichment results from deep circulation and that from a condition of high porosity. This porosity must obviously be of pre-oxidation origin, and this is one of the reasons why the distinction between oxidation and pre-oxidation cavities is of importance.

The depth of enrichment may be influenced also by the reactivity of the sulphide; for instance, Emmons assigns the thinness of the chalcocite blanket in Ducktown (Tenn.) to the occurrence there of the highly reactive pyrrhotite. But this is not the only reason for such thin enrichment, for similar blankets are found in other massive sulphide deposits consisting of the far less reactive pyrite.

Likewise, it is not impossible that the reactivity of the gangue should affect the depth of enrichment, for by decreasing the acidity it increases the rate at which pyrite and chalcopyrite are replaced by chalcocite. This again, so far as actual field results are concerned, is merely an assumption, and we cannot depend on it in planning exploration. We cannot, in fact, expect, for the present, to gain from the outcrop definite knowledge of the thickness of the enriched ore.

But these several uncertainties of projection, though real uncertainties, in no respect impair the benefits of an outcrop study. That study is intended, not to supplant, but to concentrate sub-surface exploration. With that result accomplished, it remains for such exploration to determine the effect and take the risk of the factors of projection. The poor areas are eliminated, and the good ones selected; and then, with all possible inferences used as to the shape, size and direction of the copper-bearing bodies below, the next step is the actual penetration of the bodies of rock in which ore is expected. This is a wholly different affair from the haphazard puncturing of the ground which has commonly been resorted to in disseminated copper prospects.

#### CHAPTER XIV

### SUMMARY AND CONCLUSION

The study outlined in this book was prompted by the growing difficulty of ore discovery and the need that exploration be made more efficient. The purpose of that study was the use of leached outcrop for the prediction of sulphide copper ore still hidden.

The method was that of field correlation. Because there was no systematic, previous literature, this correlation was a fresh problem whose first steps were those of finding contrasts between leached outcrop of explored copper-bearing sulphide and that of lean, pyritic ground.

Rude contrasts, usable in prospecting, rapidly emerged. Especially were these marked in the disseminated copper ores of the Southwest, and the study was confined mainly to those ores and to that region. Furthermore, though consisting in many factors, they were found to be most definite in the factor of iron precipitates formed during oxidation. Thus, the pivot of the study became these iron precipitates. Their chemistry was examined and pertinent experimentation was found to have been performed, especially by Allen, Merwin, Posnjak, Wells, and Zies.

The field correlation had shown that, in disseminated ores, the iron precipitate tended to form at the place of the sulphide when that sulphide was rich in copper; and away from the place of the sulphide when that sulphide was rich in pyrite. The distinction between indigenous and transported iron became, therefore, fundamental. The chemistry, as previously expressed in the literature, accorded with this distinction and served to indicate the "process" underlying it.

The study proceeded as a refinement and extension of this principal rule and as a search for additional rules. The relation of oxidation to water level was examined and was found to emphasize the idea that, in aerated rock, oxidation proceeds through films of water lying between sulphide and air, while in saturated rock it proceeds in a bath of water; and that, therefore, in the one instance its solutions vary greatly in concentration, while in the other they maintain an average, dilute condition. The effect of this idea is, not to yield immediate guides for prospecting, but to elucidate the processes of oxidation by limiting the alternatives of the chemistry; and through the chemistry to stimulate further observation and finally to throw light on the degree of probability of the rules developed in the field.

Another subject of more immediate application was that of the gangue; for the gangue was found to exert a significant influence on the nature of the iron precipitate. For example, in calcite, "limonite" cubes replacing pyrite were found to be common, in defiance of our principal idea that indigenous "limonite" tends to come from sulphide rich in copper. Thus, it became necessary to examine the behavior of the same sulphide in various gangues. Excepting calcite, these various gangues were thought to enter into the reaction chiefly after the oxidation of the sulphide had been completed and therefore to affect the behavior of the iron only when it had departed from the place of the sulphide. The gangue was, in fact, not found to obliterate the differences of indigenous iron precipitate corresponding to differences of sulphide. This conclusion, like the others all the way through, was first established in the field, and later fitted out with such "ideas of process" as could be developed. The empirical rule was the only part of the study directly usable in the judgment of prospects.

Furthermore, gangue was examined, not only for its influence on the nature of the iron precipitate, but also for the tendency for certain gangues to go with certain ores. Though there is no gangue which invariably means ore, yet most of the disseminated copper mineralizations are accompanied by characteristic fine-grained mixtures of minerals which survive unimpaired to the outcrop. Therefore, an outcrop lacking these minerals gives less promise for such ore.

Voids, also, were found to be usable, and in a similar way. The good disseminated ores are highly porous; a non-porous outcrop is discouraging; for copper, whether hypogene or supergene, is localized by open spaces or fissures.

The content of the outcrop in oxidized heavy metals, copper, gold, silver, arsenic, lead, and zinc, was found to have meaning especially when studied together with the gangue. Carbonate prevents the leaching of all the metals, even zinc, and a limestone wall, lying alongside or below the oxidizing orebody, sometimes precipitates these metals in oxidized form. Accordingly, if an outcrop is found still to possess carbonate, its copper has presumably not travelled significantly during oxidation. In other words, such an outcrop carrying 0.5 per cent copper presumably came from sulphide carrying not more than that amount before oxidation. With other gangues, zinc is usually, copper is often, silver and arsenic are sometimes, and gold and lead are but rarely, leached out. The principal use of gold, silver, and lead occurrences is likely to be found in cases where the sulphide ratios with these metals can be established; so that, given these metals in the outcrop, the sulphide copper content can be calculated.

Relict sulphide in the outcrop obviously constitutes a direct guide and only its scarcity prevents it from becoming more significant than the iron precipitates themselves. In correlation with those precipitates, and with other minor factors, it is an important part of the study. It is only with the aid of the relict sulphide that the iron precipitates, which are far more abundant, are given dominant significance.

This sulphide is a residuum, for some reason preserved, from a much larger quantity of sulphide previously existing. In an outcrop from a copper ore, for each grain of sulphide thus preserved, there exist many equivalent grains of "limonite." Of this problem there are two aspects. The first is, using this sulphide as a starting point, to work out empirically the significance of the "limonite" in that particular outcrop. The second, and more general, aspect is: given these scattered grains of sulphide, how truly do they represent in kind the sulphides of which they are the undestroyed remnant?

This more general aspect involves a consideration of the facts and principles of preservation. Both are difficult and not well studied. Both suggest that, given sufficient access of oxygen, all the sulphides, despite differences in reactivity, are rapidly destroyed; while, given sufficient protection, all are preserved. They indicate further that in intermediate conditions, pyrite tends to survive beyond the other sulphides; covellite and enargite are resistant, but less so; chalcopyrite, bornite, and chalcocite are still less resistant but still sometimes preserved; and sphalerite is but seldom preserved. Galena, though rapidly oxidized, is often protected by its own oxidation products.

With this subject we have finished the treatment of the minor or less specific considerations in the interpretation of outcrops. The iron precipitates, though constituting less direct evidence than relict sulphide, are much better understood and are of much more direct usefulness. The more they were studied, the more specific became the differences among these precipitates and a series of kinds was established, varying from one end at which copper-bearing sulphide is abundant to the other end at which pyrite is abundant. A sufficient number of these kinds were found meaning exclusively a particular kind of sulphide (such as coarse "limonite" boxwork meaning only mixtures of chalcopyrite and pyrite) to make it possible, where the outcrop was well

exposed, and where the sulphide was typically disseminated, to delineate in detail the sulphide ore formerly existing in the horizon of the present surface.

Thus was the sulphide reconstructed from the surface. But the problem is not to identify the places from which ore has been leached but to detect the places in which it is now hidden. This problem is one of projection outward or downward.

Throughout the study, the establishment of principles applicable to new ground and to new districts has been attempted. But, in application, it has been found that the degree of assurance rapidly dwindles with distance from the place where the principle is proved to hold. In judging a prospect, it is safer to learn, by gradation to actual sulphide, the meaning of kinds of "limonite" within that ground, or under similar conditions nearby, than it is to bring in rules from another district. The best guide is a habit locally derived.

This study has yielded definite guides only to disseminated ore, from which iron is not significantly leached during oxidation, and in which volume change is unimportant. But as these ores become exhausted, our interest must lie increasingly in ore that is more easily missed and this study, if it is to play its maximum part, must advance more and more toward the aggregated end of the series, in which iron is lost and volume is changed.

The study so far accomplished, then, may be regarded as a foothold in the problem of leached outcrops as guides to copper ore. The result has been definite but limited in range and from this result, excursions are now needed into other parts of the problem, covering not only capping but also gossan. That such excursions can be made, and that, through the effort of qualified workers, phenomena now in a state of confusion can be brought into an orderly display, is, in the light of present progress, a reasonable expectation.

#### GLOSSARY

Aggregated sulphide. Massive sulphide.

Borgströmite. A basic ferric sulphate of composition, 3Fe<sub>2</sub>O<sub>3</sub>·4SO<sub>3</sub>·9H<sub>2</sub>O<sub>4</sub> Capping. The oxidized equivalent of disseminated sulphide material.

Contiguous "limonite." "Limonite" in the gangue around and adjoining a cavity or group of cavities formerly occupied by iron-bearing sulphide. Within diffusion distance (about 1 cm.) of the cavities. Formed when the gangue begins to participate strongly in the reactions and as the next step beyond indigenous limonite.

Disseminated sulphide. Sulphide scattered as specks and veinlets through rock and constituting not over 20 per cent of the total volume.

Exotic "limonite." "Limonite" precipitated in rock other than that which formerly contained the iron-bearing sulphide. The iron has travelled by circulation and may have moved tens of feet away from its original sulphide source.

Gossan. The oxidized equivalent of aggregated sulphide material.

Indigenous "limonite." "Limonite" precipitated within the same cavity or group of cavities in which the sulphide source of the iron formerly existed. Although the iron may have travelled as much as 1 cm. across intervening gangue, that gangue has reacted too slowly to participate in the reactions, and the reaction has proceeded as though the dissolved iron and its precipitant were in contact within the cavities.

"Limonite." Used in this book in quotation marks to indicate fine grained, unidentified ferric precipitates. There is no mineral species of this

Metore. A term including both capping and gossan. After ore. Cf.

meta-andesite, protore.

Transported "limonite." "Limonite" precipitated outside the cavity or group of cavities in which it originated. Includes both contiguous and exotic "limonite."



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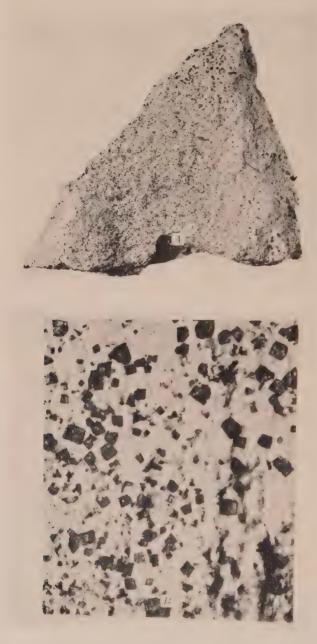
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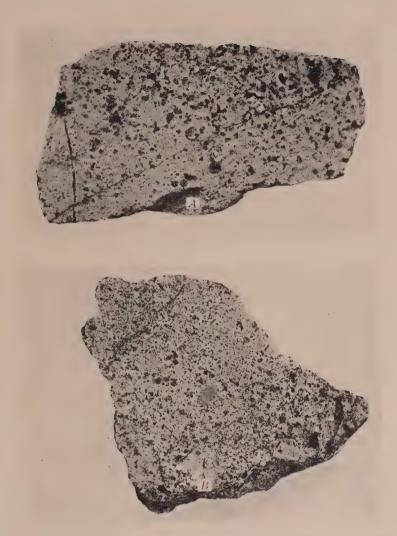


A. Specks of "limonite" in cavities formerly occupied by sulphide. Actual size.

B. Same. × 10. (Photos by United States Geological Survey.)



A. Similar to I-A but with more "limonite." Actual size. B. Same.  $\times$  5. (Photos by United States Geological Survey.)



A. "Limonite" in cavities formerly occupied by sulphide, with minor "limonite" soaked into gangue. Actual size. (See p. 145.)

B. Similar to III-A. (Photos by United States Geological Survey.)
(See p. 146.)

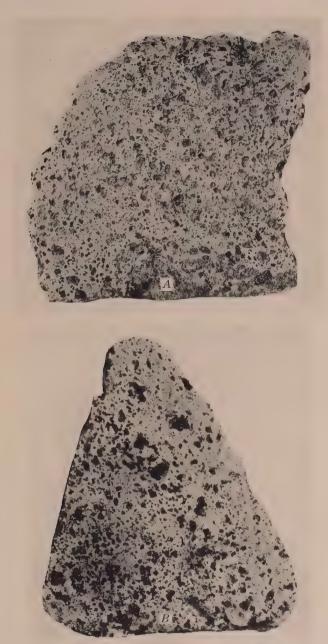
PLATE IV





A. Similar to III-A but with more "limonite." Actual size. (See p. 147).

B. Similar to III-A but with still more "limonite." Corresponds to rich ore. Actual size. (See p. 147). (Photos by United States Geological Survey.)



A. Areas corresponding to former feldspar phenocrysts stained with "limonite" derived from tiny grains of sulphide formerly within the phenocrysts. These grains are now represented by clusters of tiny pits carrying a small amount of "limonite." Actual size.

B. Similar to V-A but with more "limonite" and with the "limonite" less confined to phenocrysts. Actual size. (Photos by United States Geological Survey.)



Same as V-B.  $\times$  10. The pits from which sulphide has been removed are visible as black spots within the stained areas. (Photo by United States Geological Survey.)



A and B. "Limonitic" halos surrounding cubical pits from which pyrite has been removed. An unstained zone, in some cases, lies between the halos and the pits. Actual size.

C. Kaolinic rock flooded with "limonite" excepting in halos immediately surrounding cubical pits. Actual size. (Photos by United States Geological Survey.)





A. Quartz sponge made by the removal of pyrite during oxidation. The core still carries pyrite. Actual size. (See p. 76).

B. "Limonite" sponge made, like bog iron ore, by the compacting of leaves of "limonite" deposited at a distance from the sulphide-source of the iron. Actual size. (Photos by United States Geological Survey.)

LEACHED OUTCROPS PLATE IX



Siderite boxwork made by replacement of limestone underlying an oxidizing pyritic body. Actual size. (See p. 54.) (Photo by United States Geological Survey.)



Crusts of "limonite" encroaching on a limestone nucleus. Actual size. (Photo by United States Geological Survey.)

LEACHED OUTCROPS PLATE XI

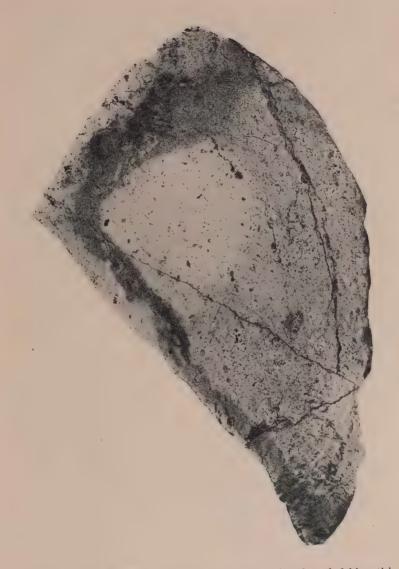


Tucson, Arizona. "Surface crackling." 1/25



A and B. Tyrone, New Mexico. The "mantle of debris." 1/25 (Photo by Blanchard.)

LEACHED OUTCROPS PLATE XIII



Tyrone, New Mexico. "Surface hardening" in altered feldspathic porphyry. Actual size. (Photo by United States Geological Survey.)



Uncle Sam Mine, Bisbee, Arizona. A porphyry breccia made by the shrinkage during oxidation of a sulphide orebody below, and cemented by calcite. (Photo by Kingsbury.)

LEACHED OUTCROPS PLATE XV



A surface of "relief" "limonite."  $\,\times\,10.\,$  (Photo by United States Geological Survey.)





A. A copper bearing 'limonite'' 'pitch'' replacing chalcopyrite along cracks. A stage in the formation of 'limonite' boxwork. Actual size. (See p. 124.)

B. Same. × 4. (Photos by United States Geological Survey.)

LEACHED OUTCROPS PLATE XVII

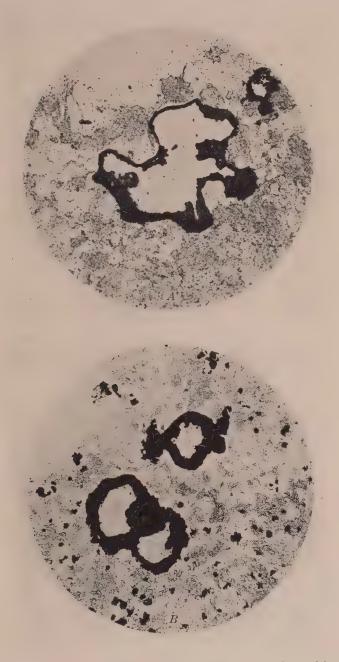


Fine "limonite" boxwork from chalcopyrite.  $\times$  10. (See p. 125.) (Photo by United States Geological Survey.)



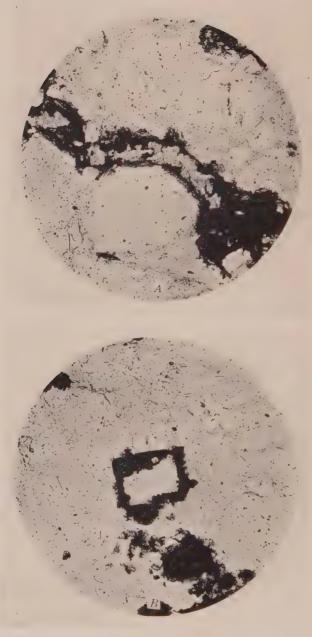
A. Coarse "limonite" boxwork replacing chalcopyrite. Actual size. (See p. 127.)
B. Coarse "limonite" boxwork replacing chalcopyrite which occurred in large blebs in quartz. Actual size. (See p. 127.) (Photos by United States Geological Survey.)

PLATE XIX



A. Morenci, Arizona. Hematite rims without halos, in cavities left by removal of sulphide grains. That interiors are actually empty is proved by study of freshly broken hand specimens with binocular microscope. No iron oxide in gangue. The structure is intermediate between that of "relief" hematite and that of compact hematite rims. × 125. (Tunell.)

B. Morenci, Arizona. Hematite rims [without halos. Spherulites of hematite replacing gangue. X 125. (Tunell.)



A. Morenci, Arizona. Veinlet lined with hematite and filled with jarosite. × 125. (Tunell.)

B. Morenci, Arizona. Hematite lining, without halo, of cavity made by removal of pyrite. × 125. (Tunell.)

LEACHED OUTCROPS PLATE XXI



A. Morenci, Arizona. Hematite rims with halos of thin hematite plates in sericite cleavage spaces.  $\times$  125. (Tunell.)
B. Morenci, Arizona. Hematite rim: pepper of hematite spherulites spreading into adjoining phenocryst.  $\times$  50. (Tunell.)

PLATE XXII



Morenci, Arizona. Hematite rim with halo of thin hematite plates in sericite cleavage spaces.  $\times$  285. (Tunell.)

LEACHED OUTCROPS PLATE XXIII



A. Tyrone, New Mexico. Halos of hematite and goethite spherulites in gangue around cavities left by sulphides.  $\times$  50. (Tunell.)
B. Morenei, Arizona. Disseminated jarosite crystals replacing "chloritic" porphyry.  $\times$  125. (Tunell.)



A. Morenci, Arizona. Disseminated hematite spherulites replacing gangue. × 50. (Tunell.)

B. Tyrone, New Mexico. Corner of phenocryst replaced by jarosite. × 125. (Tunell.)

### Sans Tache



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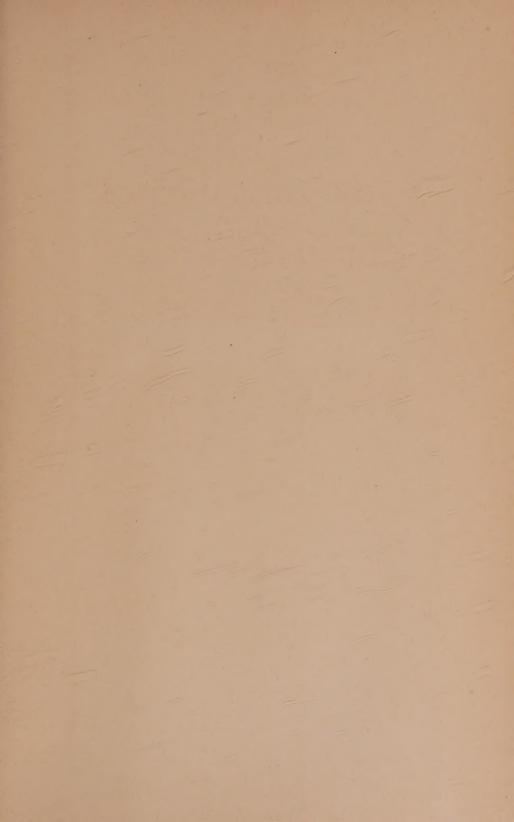
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